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Air Emission Monitoring

LAND DISPOSAL TOXIC AIR EMISSIONS

EVALUATION GUIDELINE

Office of Solid Waste

U.S. Environmental Protection Agency

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This manual presents a procedure for assessing the impact of Hazardous Air Emissions from disposal facilities on the downwind population.

The report is prepared to provide the facility owner or operator and the permit writer guidance on evaluating the performance of facility design, and preparation and analysis of the permit application. The manual will also provide a quantitative tool for the rational evaluation of hazardous air emissions from land disposal facilities, and for prediction of Ambient air quality of hazardous waste components.

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FOREWORD

This manual presents a procedure for assessing the impact of hazardous air emissions from disposal facilities on the downwind population. The disposal facilities considered in this document include surface impoundments, seepage facilities, landfills, and land treatment facilities. The application of the procedure may be extended to waste piles depending upon the similarity of air emissions routes and the characteristics of the emitting surface in contact with the atmosphere. These facilities will hereinafter be referred to as disposal facilities or land disposal facilities.

The report is prepared to provide the facility owner or operator and the permit writer guidance on evaluating the performance of facility design, and preparation and analysis of the permit application. The manual will also provide a quantitative tool for the rational evaluation of hazardous air emissions from land disposal facilities, and for prediction of ambient air quality of hazardous waste components.

Chapter 2 presents the method of estimating the hazardous air emission rates from disposal facilities. Chapter 3 describes a screening technique for predicting ambient air quality. The preliminary evaluation by the screening technique will form a basis for requiring a more sophisticated evaluation of the impact of the disposal facilities.

Chapter 4 is an attempt to gather data on the present background concentrations of hazardous chemicals in urban and rural ambient air. The background concentration will affect the extent of emission control required for prevention of adverse health effect on the downwind public. A logical source of such information would be site-specific monitoring

data. The data properly taken around a disposal site will provide a basis for performing an ultimate test of comparing the predicted with actual result. The example calculations presented in Chapter 6 will serve as a quick reference for the use of the analytical techniques.

This report was completed around mid-December, 1980, as a part of documents to support proposed regulations which will be published in the Federal Register in February, 1981.

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INTRODUCTION

1.1 Purpose

This guidance manual is prepared to present a brief description of technical information that can be used in evaluating the potential of emissions of volatile hazardous chemicals into the atmosphere from land disposal facilities. The land disposal facilities include surface impoundments, seepage facilities, landfills, and land treatment facilities. The method for predicting the impact of the facility on ambient air quality essentially consists of two step processes; first, it requires estimation of emission rates of toxic components from a land disposal facility; second, this information is in turn used for air dispersion modeling to predict the ambient air quality.

1.2 Content Description

The dispersion modeling technique is rather general to the extent that it is applicable to area sources of which land disposal facilities are a type. The estimation of emission rates, however, requires a particular method that is suited to each application of land disposal facilities. Although waste piles are not specifically covered in this report, it is believed that one of the methods (most likely the land treatment model) may be used for the estimation of volatile emissions from waste piles based on the similarity of transport routes and configuration. In all cases the estimation method for the emission rates addresses volatile constituents in the waste. The particulate matter emissions are generally derived from the expression of "emission factors", but this aspect of emission rate estimation is not addressed in this report.

The techniques presented here are predictive models, and do not involve the methods of actual measurements. However, the methods of performing measurements of emission rates as well as ambient air concentrations of waste constituents have been established, and these measurements may be effectively used to verify the accuracy of the prediction.

The land disposal facility should be designed, maintained and closed in a manner which will not impair post-closure uses of the land and soil, and public health will not be endangered due to air emissions and water infiltration. The procedure presented here will allow one to make a preliminary evaluation on the adequacy of design for a disposal facility from a standpoint of atmospheric dispersion of volatile hazardous chemicals. The evaluation examples will serve as a quick reference problem for estimating the emission rates and for comparing the estimated concentrations with the permit provisions. The approach to arriving at allowable ambient air concentrations will be presented in a Permit Writers Guidance Manual which will expand the material contained in Chapter IV of the manual.

The evaluation procedure can be used to check the adequacy of the facility design to minimize the potential of air emissions of hazardous substances as necessary to protect public health.

The main body of the report will address various models needed for the evaluation and predictions. Specific examples are shown in a later chapter to facilitate their use.

1.3 Use of Other Manuals

EPA has published a number of technical resource documents and manuals to support recently proposed RCRA regulations. Each document

supports the appropriate area of concern. But some documents also contain references and a brief description of the subject matter related to air emissions. These documents and manuals include:

- Management of Hazardous Waste Leachate
- Guide to the Disposal of Chemically Stabilized and Solidified Wastes
- Closure of Hazardous Waste Surface Impoundments
- Design and Management of Hazardous Waste Land Treatment Facilities
- Soil Permeability Test Manual
- Leachate Characterization from a Hazardous Waste Facility
- Landfill Closure Manual
- Ground-Water Monitoring for Owners and Operators of Treatment, Storage or Disposal Facilities
- Landfill and Surface Impoundment Performance Evaluation
- Evaluating cover Systems for Solid and Hazardous Waste
- Guide to the Disposal of Chemically Stabilized and Solidified Wastes
- Hydrologic Simulation on Solid Waste Disposal Sites
- Management of Hazardous Waste Leachate
- Lining of Waste Impoundment and Disposal Facilities
- Design and Management of Hazardous Waste Land Treatment Facilities.
- Closure of Hazardous Waste Surface Impoundments.

This manual is not directly related to any of the above manuals. However, the reader is encouraged to consult the above documents for any materials relevant to the evaluation of air emissions.

The predictive models presented in this manual are based on the best information currently available in the literature. The correlations pertaining to the estimation of volatile emissions from surface impoundments are presently being tested in the field using the "concentration profile technique." In the models for estimating emissions from covered landfills, the diffusion in soil pore is considered a rate controlling step. The effect of barometric pumping and thermal diffusion on the rate of emissions has been mentioned in the literature. But the information is lacking on importance of these phenomena in comparison with diffusion controlling transport. The land treatment model is rather a recent endeavor and would require further experimental verification to identify all parameters affecting air emissions and to substantiate its accuracy.

The techniques of measuring air emission rates and of monitoring ambient air concentrations of specific chemicals are beyond the scope of this manual and are not presented here.

II. ESTIMATION OF EMISSION RATES FROM DISPOSAL FACILITIES

1) Surface Impoundments

In order for the hazardous compound in the waste to be emitted into the atmosphere, the following three elementary processes must occur:

1. The hazardous compound in the surface impoundment must travel to the surface where it is in contact with the atmosphe

2. At the surface(or liquid-air interface), the hazardous compound must vaporize or establish the vapor liquid equilibrium which determines its concentration in the air phase in the immediate vicinity of the surface based on the concentration in the liquid phase at the surface.

3. Once vaporized at the interface, the hazardous component must be transported into the bulk of the air stream.

In the transport of the hazardous component in the liquid and air phases corresponding to steps 1 and 3 above, it encounters inherent resistances. If a pure volatile liquid is vaporized into the atmosphere, the resistance for steps 1 and 2 is zero, and only the resistance in the air phase (step 3) is controlling. On the assumption of no resistance for mass transfer rate in Step 2, the science of "thermodynamics" can be used to quantify the equilibrium phenomena. The mass transfer coefficients (k_L, k_g) expressed in a unit of gr-mol/cm^2·sec can also be expressed in units of #-mol/ft^2·hr, cm/sec, or 1/day. The method of conversion is shown in the examples. The reciprocals of the resistances encountered in steps 1 and 3, or mass tansfer coefficients are designated by

k_L : liquid phase mass transfer coefficient(step 1 above), gr-mol/cm^2·sec.

k_g : gas phase mass transfer coefficient(step 3 above), gr-mol/cm^2·sec.

In addition to the volatilization of the hazardous component, other processes would occur simultaneously in the surface impoundment. Engineers are often concerned with biodegradation, transport through soil, outflow in the effluent and sludge, and accumulation. Quantitatively, one can write the following material balance for the amount of a hazardous substance being transported and transformed:

Input = Output* + Biodegradation + Air Emissions + Transport through Soil + Accumulation

Our primary concern is the air emissions. The rate of air emissions of a hazardous substance, i, is expressed by**

$$Q_i = K_L \cdot A\,(x_i - x_i^*)\,,\ MW_i \qquad (1)$$

where Q_i : rate of air emissions of a component i, gr/sec.

K_L : overall mass transfer coefficient(expressed in the liquid phase concentration), gr-mol/cm^2·sec

A : area of surface impoundment, cm^2

x_i : concentration of component i in the impounded liquid, mole fraction

---

* Output includes the amount in the effluent and sludge.

** The correct formula is $Q_i - y_i(Q_i + Q_j) = K_L\,A\,(x_i - x_i^*)$ where y_i is the mole fraction of the component i in the air phase. Since $Q_j = 0$ (subscript j refers to air), and $(1-y_i) \cong 1$ for low air emissions, Equation (1) results.

x_i^* : liquid-phase concentration of component i in equilibrium with the air phase concentration of component i, mole fraction

MW_i : molecular weight of hazardous component i.

In Equation (1) K_L is the reciprocal of the overall resistance atrributable to the sum of individual resistances. The method of combining the individual mass transfer coefficients is well established.

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{K \cdot k_g} \qquad (2)$$

where K is the constant establishing the equilibrium between the liquid and air phases expressed by $y_i = K\, x_i$, and y_i is the mole fraction of component i in the air phase. There are several ways of determining the values of K (K-values) for use in Equation (2). There is a compilation of the results of the vapor-liquid equilibrium experiments, and Henry's law constants, from which the K-values can be calculated. The K-values can also be determined from Racult's law and the activity coefficient concept. Detail methods on the evaluation of the K-value are beyond the scope of this report. For a brief summary, the reader may consult the appendix.

It is commonly assumed that the concentration of component i in the air stream is negligible compared with that in the liquid phase, that is $x_i^* = 0$ in Equation (1). Hence an adequate expression for the emission rates from the surface impoundment is

$$Q_i = MW_i \cdot K_L \cdot A \cdot x_i \qquad (3)$$

In order to calculate the emission rates using Equation (3),

the overall mass transfer coefficient must be known. The mass transfer coefficients, k_L and k_g, in the liquid and air phases are correlated and reviewed by various experimenters in academic institutions, and industries (7) (22). The results are summarized below

1. Surface impoundment retaining natural surface

a. liquid-phase mass transfer coefficient

$$k_L = (11.4 Re^{*0.195} - 5) \frac{D_{i,H_2O}}{D_{Tol,H_2O}} \quad \text{, by Cohen(4)} \qquad (4)$$

$$k_L = 5.78(1.024)^{\theta-20} U_o^{0.67} H_o^{-0.85} \frac{D_{i,H_2O}}{D_{O_2,H_2O}} \quad \text{, by Owens (13)} \qquad (5)$$

b. gas-phase mass transfer coefficient

$$k_g = 0.0958 U_{air}^{0.78} N_{sc}^{-0.67} d_e^{-0.11} \frac{\rho_{air}}{MW_{air}} \quad \text{, by MacKay(11)} \qquad (6)$$

2. Surface impoundment aerated by the mechanical surface aerator

a. liquid-phase mass transfer coefficient

$$k_L a_V V = \frac{J\ (POWR)\ (1.024)^{\theta-20}(\alpha)\ (10^6)}{165.04} \frac{D_{i,H_2O}}{D_{O_2,H_2O}},$$

by Thibodeaux (16) (7)

b. gas-phase mass transfer coefficient

$$k_g = 0.00039 \frac{\rho_g D_{i,air}}{d} (N_{Re})^{1.42} (N_{FR})^{-0.21} (N_p)^{0.4} (N_{SC})^{0.5},$$

by Reinhart (14) (8)

When the air emissions from the non-wastewater surface impoundment need to be estimated, the ratio of the diffusion

(Note: In the correlations given by Equations (4) - (8), the mass transfer coefficients k_L, k_g, are expressed in lb-mol/ft^2·hr. The conversion to gr-mol/cm^2·sec is straightforward.)

coefficients of component i in water in Equations (4 or 5) and (7) should be replaced by the diffusion coefficients in the solvent to calculate the liquid-phase mass transfer coefficients. Other investigators recommend the use of the relationship (15)(18),

$$\frac{D_i \text{ in a solvent}}{D_j \text{ in a solvent}} = \left(\frac{MW_j}{MW_i} \right)^{0.5} \qquad (9)$$

The similar relationship has been used for the approximation of the gas-phase diffusivity ratios. Kyosai compares the experimental results with the ratios of molar or critical volumes in relationship to the diffusivity equation proposed by Wilke and Chang (24).

The emission rates of volatiles from the surface impoundment could be seasonal due to the seasonal temperature variation. The correction to the temperature variation can be incorporated in the evaluation of the mass transfer coefficients by recognizing the factors dependent upon the temperature. There are explicit terms for the temperature correction in the correlations of the mass transfer coefficients. The dependence of the diffusion coefficients upon temperature can be accounted for noting that the gas phase diffusivity is proportional to temperature by 1.5 power and the liquid phase diffusivity is directly proportional to temperature.

For a given surface impoundment, the individual mass-transfer coefficients for various compounds can be simplified by refering to a typical compound whose base values are known or easy to evaluate. Several experimenters (13), (15), (16) used oxygen as reference compound for the liquid phase mass transfer, and water vapor as reference compound for the air phase mass transfer. Upon taking the ratios of Equations(4 or 5), (6), (7), and (8) and considering the temperature effect with respect

to a reference compound and temperature(25°C used in the present example below), one can obtain

1. Natural surface impoundment

a. liquid-phase

$$k_{L,i} = \left(\frac{MW_{O_2}}{MW_i} \right)^{0.5} \left(\frac{273 + \theta}{298} \right) k_{L,O_2} \qquad (10)$$

b. gas-phase

$$k_{g,i} = \left(\frac{MW_{H_2O}}{MW_i} \right)^{0.335} \left(\frac{273 + \theta}{298} \right)^{1.005} k_{g,H_2O} \qquad (11)$$

2. Aerated surface impoundment

a. liquid-phase

$$k_{L,i} = \left(\frac{MW_{O_2}}{MW_i} \right)^{0.25} \left(\frac{1.024^{\theta-20}}{1.024^{5}} \right) \left(\frac{273 + \theta}{298} \right)^{0.5} k_{L,O_2} \qquad (12)$$

b. gas-phase

$$k_{g,i} = \left(\frac{MW_{H_2O}}{MW_i} \right)^{0.25} \left(\frac{298}{273 + \theta} \right)^{0.92} k_{g,H_2O} \qquad (13)$$

The liquid phase mass transfer coefficients for oxygen and the gas-phase mass transfer coefficients for water vapor are calculated using Equations (5), (6), (7), and (8), and listed on Table 1. The convective liquid-phase mass transfer coefficients calculated by Equation (4) is 4.2×10^{-5} gr-mol/cm^2·sec in comparison with 2.4×10^{-3} gr-mol/cm^2·sec calculated by Equation (5). The former represents the results obtained from the wind tunnel experiments, and the latter is for free flowing stream. The conservative number is used. The liquid-phase and gas phase mass transfer coefficients for all substances

of concern can be calculated individually by Equations (4) through (8), or more simply by Equations (10) through (13). The experimental and calculated mass transfer coefficients for O_2 in the liquid phase and H_2O in the air phase is needed to use Equations (10) - (13). The field measurement values in the literature are comparable to these values (15) (22).

Table 1. Mass Transfer Coefficients for Reference Compounds (25°C)

	Natural Surface	Turbulent Surface
k_L (gr-mol/cm^2·sec)	2.4×10^{-5}	0.12
(O_2 in water)	0.18(lb-mol/ft^2·hr)	866.2(lb-mol/ft^2·hr)
k_g(gr-mol/cm^2·sec)	2.7×10^{-5}	4.6×10^{-4}
(H_2O in air)	0.2(lb-mol/ft^2·hr)	3.41(lb-mol/ft^2·hr)

Care must be taken in estimating the emission rates from the aerated surface impoundment, particularly the activated sludge process. It can be visualized as consisting of two distinct zones where emissions occur. One zone is the core of aeration where the mass trnasfer coefficients calculated by Equations (7) and (8) are applicable. Beyond a certain region of turbulence caused by aeration, the turbulence diminishes. The air emissions are comparable to the natural surface impoundment, and the mass transfer

coefficients for the second zone can be calculated by Equations (4 or 5), and (6). The emission rates from the turbulent and convective zones must be summed to obtain the overall emission rates from an aerated surface impoundment (7). It can be shown that in order to use Equation (3) the area-averaged overall mass transfer coefficients give identical answers:

$$K_L = (K_L)_c \frac{A_c}{A} + (K_L)_T \frac{A_T}{A} \qquad (14)$$

In Equation (14) K_L is the area-averaged overall mass transfer coefficient to be used in Equation (3) for the aerated surface impoundment, $(K_L)_c$ is the overall mass transfer coefficient for the convective region, $(K_L)_T$ is the overall mass transfer coefficient for the turbulent region, A_c is the effective surface area of the convective region, A_T is the effective surface area of the turbulent region, and A is the total surface area of the aerated surface impoundment. A_c/A and A_T/A represent the fractions of the convective and turbulent surface areas, respectively.

2) Landfills

The approach to estimation of air emissions from landfills presented here is an extension of the study on hexachlorobenzene emissions from landfills undertaken under the EPA contract(7). The estimation method described by Farmer is based on the diffusional process in the soil pore. Additional emissions of air pollutants caused by generation of gases in soil are shown by Thibodeaux (17) to be a significant portion of air emissions when the hazardous

waste is landfilled with gas-generating wastes such as domestic garbage.

Farmer et. al presented a method of estimating the emission rate from landfills based on the controlling mechanism of diffusion through soil. Chemical vapors originated from hazardous waste move upward by molecular diffusion until the vapors reach the air-soil interface. The rate of air emissions at steady state is expressed by

$$q_i = -D_L \frac{P_a^{10/3}}{P_T^2} \frac{(C_{io} - C_i^*)}{h} \qquad (15)$$

where q_i is the rate of emissions of component i per unit area, $gr/cm^2 \cdot sec$, D_L is the diffusion coefficient of component i, cm^2/sec, P_a is air-filled porosity, cm^3/cm^3, ($P_a = 1 - \rho_B/2.65 - w \cdot \rho_B$), ρ_B is the soil bulk density, gr/cm^3, w is the soil water content, gr/gr, P_T is the total porosity, cm^3/cm^3, ($P_T = 1 - \rho_B/2.65$), h is the depth of soil cover, cm, C_{io} is the concentration of component i at the soil-air interface, gr/cm^3, C_i^* is the concentration of component i in the air space at the immediate vicinity of the waste(or in equilibrium with the waste), gr/cm^3.

Thibodeaux presented the following simple expression to incorporate the long-term values for the site-specific soil conditions (17).

$$q_i = -K_{G,i} (C_i - C_i^*) (2.44 \times 10^4) \qquad (16)$$

where 2.44×10^4 is the molar volume of gas, $cm^3/gr\text{-}mol$, $K_{G,i}$ is the overall

mass transfer coefficient(expressed in the gas phase concentration), gr-mol/cm^2·sec, and C_i is the concentration of component i in the air far away from the soil-air interface. The overall mass transfer coefficient is expressed by

$$\frac{1}{K_{G,i}} = \frac{1}{k_{s,i}} + \frac{1}{k_{g,i}} \qquad (17)$$

where $k_{s,i}$ is the soil phase mass transfer coefficient of component i (expressed in the gas phase unit), gr-mol/cm^2·sec, or $k_{s,i} = D_i \cdot \epsilon / (h \cdot \tau \cdot 2.44 \times 10^4)$ ϵ is the porosity of the cover material, τ is the tortuosity, and $k_{g,i}$ is the air phase mass transfer coefficient, gr-mol/cm^2·sec.

It has been shown that the resistance to air emissions in the air phase is negligible compared with that in the soil phase (17). Equation (16) can be used with $C_i = 0$ for all practical purposes.

The diffusion coefficient in the gas phase is dependent upon the type of the compound, and temperature, and can be related to the variation of molecular weight and temperature by the following proportionality relationship (7) (18).

$$D_i \propto \left(\frac{1}{MW_i}\right)^{0.5} (T)^{1.5} \qquad (18)$$

or

$$D_i = \left(\frac{MW_1}{MW_i}\right)^{0.5} \left(\frac{T}{T_1}\right)^{1.5} D_1 \qquad (19)$$

where MW_i is the molecular weight of component i, gr/mol, and T is temperature, ^{o}K. For matter of choice, a temperature of $298^{o}K$ is used for T_1, and $D_1 = 0.088$ cm^2/sec for benzene is used(MW=78.1). Equation (19) becomes

$$D_i = 1.5 \times 10^{-4} \left(\frac{1}{MW_i} \right)^{0.5} T^{1.5} \qquad (20)$$

It is convenient to use the partial pressure of a hazardous component in the vapor space in place of the equilibrium concentration. One can express

$$C_i^* = \frac{p_i^* MW_i}{RT} = \frac{\gamma_i P_i^{\circ} MW_i}{R T} x_i \qquad (21)$$

where p_i^* is the partial pressure of component i in equilibrium with the waste, mmHg, and R is the gas constant, $(62{,}363\ cm^3 \cdot mmHg/^{o}K \cdot mol)$. The emission rate of a hazardous component from a landfill can be estimated with the use of Equations (15), (20), and (21), or (16) and (17). Information needed for the estimation includes the porosity, moiture content, and bulk density of cover soil, the partial pressure of component i in equilibrium with the waste, the cover thickness, the molecular weight of the component, temperaure, and the landfill area.

The soild waste landfilled with the hazardous waste is subject to the biological process occuring in soil, and generates gases due to anaerobic processes. The convection caused by the generated gases carries volatile chemicals toward the surface of soil. Thibodeaux (17) incorporated the transport mechanism

to account for the air emissions resulting from the moving gas. The equation presented for the rate of air emissions is

$$q_i = \bar{V} \frac{C_i^* - C_{io}}{\exp\left(\frac{h \cdot \bar{V} \cdot \tau}{D_i \cdot \epsilon}\right) - 1} + \bar{V} C_i^* \qquad (22)$$

where $\bar{V}$ is the average gas velocity in the soil pore in the upward direction, cm/sec. In order to obtain the concentration of component i at the soil-air interface, C_{io}, the air-phase mass transfer given below by Equation (23) should be utilized,

$$q_i = - k_{g,i} (C_{i\infty} - C_{io}) \, 2.44 \times 10^4 \qquad (23)$$

Equations (22) and (23) should be solved simultaneously to estimate the emission rates from a landfill with gas generation. Several examples of using Equations (22) and (23) are given in the example section.

The comparison between Equations (15) and (16) shows that the porosity and the air-filled porosity are related by

$$\epsilon = 1.73 \frac{P_a^{10/3}}{P_T^2} \qquad (24)$$

There are other transport processes which will add to air emissions. Several investigators are concerned with the effect of barometric pumping and thermal diffusion caused by temperature gradient across the soil. It appears that the role of these processes is insignificant compared with the overall emissions. Hence these additional emissions are not considered in this report.

Synthetic material is often used as a cover material. Farmer expresses the effectiveness of the synthetic material in retarding the volatilization and movement of chemical vapors in terms of the equivalent thickness of soil (25). He presented a graph wich correlates polyethylene thickness (h_f, cm) in terms of the equivalent thickness of soil ($h_{eq.}$, cm) corresponding to a bulk density (ρ_B) of 1.19 gr/cm^3 and a soil water content (w) of 0.2 gr/gr. This correlation can be presented by the following equation:

$$h_{eq} = 134.6\ h_f \qquad (25)$$

When synthetic material and soil are used together in layers, their individual resistances to air emissions are additive. Equation (15) can be rewritten as

$$q_i = D_i \left[\frac{1}{\frac{h}{P_a^{10/3}/P_T^2} + \frac{h_{eq}}{P_{a1}^{10/3}/P_{T1}^2}} \right] C_i^* \qquad (26)$$

where P_{a1} and P_{T1} are the air-filled porosity and the total porosity, respectively, used in obtaining the equivalent soil thickness. The data presented by Farmer can be used to evaluate the values of P_{a1} and P_{T1} as follows:

$$P_{T1} = 1 - \frac{1.19}{2.65} = 0.551$$

$$P_{a1} = P_{T1} - (0.2)(1.19) = 0.313$$

Then Equation (26) becomes

$$q_i = D_i \left[\frac{1}{\frac{h}{P_a^{10/3} / P_T^2} + \frac{134.6\ h_f}{0.313^{10/3} / 0.551^2}} \right] C_i^* \qquad (27)$$

or

$$q_i = D_i \left[\frac{1}{\frac{h}{P_a^{10/3} / P_T^2} + 1962.8\ h_f} \right] C_i^* \qquad (28)$$

Similarly, the estimation of air emission rates from a landfill covered by soil and polyethylene film with internal gas generation can be made by

$$q_i = \bar{V} \frac{C_i^* - C_{io}}{\exp\left[\frac{\bar{V}}{D_i}\left(\frac{h}{P_a^{10/3}/P_T^2} + 1962.8\ h_f\right)\right] - 1} + \bar{V}\ C_i^* \qquad (29)$$

3) Land Treatment Facilities

There is very limited information with regard to models and experimental data dealing with air emissions during land treatment operations. Recent experimental results sponsored by API indicate that important variables significantly affecting air emissions include soil type, humidity, and loading rate. These experiments are carried out on a laboratory scale using

oily sludges generated in refineries. Other factors under study are temperature, air velocity, and mode of application. The sludges are applied into soil by surface spreading and subsurface injection.

The rate of emissions at time t (sec.) after the application of the waste by surface spreading or subsurface injection can be expressed by*

$$q_i = \frac{D_{ei}\, C_{ig}}{\left[h_s^2 + \frac{2\, D_{ei}\, t\, A(h_p - h_s)\, C_{ig}}{m_{io}} \right]^{1/2}} \qquad (30)$$

where q_i is the rate of emission of component i, $gr/cm^2 \cdot sec$, D_{ei} is the effective diffusivity of component i in the air-filled soil pore, cm^2/sec, m_{io} is the initial amount of component i placed for land treatment, gr, h_s is the depth of subsurface injection, cm, h_p is the depth of soil contamination below the soil surface, cm(assumed to be 5 - 6 inches = 12.7 - 15.24 cm), A is the surface area of waste application, cm^2, C_{ig} is the gas-phase concentration of component i at the oil-gas interface in the soil pore, gr/cm^3.

The concentration of component i in the gas side of the interface, C_{ig}, can be determined by (See the appendix for derivation)

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* See the appendix for detailed derivation supplied by Thibodeaux. This model has not been verified experimentally except the API's preliminary data.

$$C_{ig} = \left[\frac{H_c}{1 + H_c \dfrac{6\, D_{ei}\, z_o}{D_{wi}\, a_s (h_p^2 + h_p\, h_s - 2\, h_s^2)}} \right] C_{iwo} \qquad (31)$$

where H_c is the Henry's law constant in concentration, C_{iwo} is the initial concentration of i in the oily waste, gr/cm^3, z_o is the oil layer diffusion length, cm, D_{wi} is the effective diffusivity of i in the waste, cm^2/sec, and a_s is the interfacial area per unit volume of soil, cm^2/cm^3.

The average emission rate over the evaporation life-time t_d sec can be obtained by integrating Equation (30) and dividing with respect to time, which yields

$$\bar{q}_i = 2\, q \quad \text{at } t = t_d \qquad (32)$$

where t_d is the dry-out time, sec, to be determined by

$$t_d = \frac{(h_p + h_s)}{2\, D_{ei}\, C_{ig}} \left(\frac{m_{io}}{A} \right) \qquad (33)$$

The path length of diffusion through the film and lump type of oil in soil can be estimated from

$$z_o = \frac{d_p\, \bar{\rho}_p\, w_f}{6\, \bar{\rho}_w} \quad \text{for film form oil} \qquad (34)$$

$$z_o = \frac{d_p}{2} \quad \text{for lump form oil} \qquad (35)$$

where d_p is the soil clump diameter, cm, $\bar{\rho}_p$ is the soil clump density (2.65 gr/cm^3), w_f is the fraction of oil in film form

on the soil, and $\bar{\rho}_w$ is the waste oil density, gr/cm^3. The interfacial area is

$$a_s = 6/d_p \text{ for film} \qquad (36)$$

$$a_s = 2.7/d_p \text{ for lump} \qquad (37)$$

The mass fraction of oil in the film form can be estimated by

$$w_f = \frac{0.5\ M_T}{h_p\ \bar{\rho}_B\ A} \qquad (38)$$

where $\bar{\rho}_B$ is the bulk soil density, gr/cm^3, and M_T is the total application amount of waste, gr. The example calculations given later will facilitate the use of the above equations.

Volatile wastes are incorporated into soil for land treatment by subsurface injection. This method of application reduces volatilization in comparison with surface spreading, and bring the waste in intimate contact with microbia in soil. The depth of subsurface injection is 5 - 6" in the commercial practice.

III. AMBIENT AIR QUALITY MODELING FOR AREA SOURCES (5)

Hazardous substances evaporated into the atmosphere from disposal facilities may introduce significant impacts on human health and the environment in the surrounding region. We will consider the use of air quality modeling to assess whether emission reductions are necessary to avoid exceeding acceptable levels of hazardous substances.

Once a maximum acceptable concentration for a hazardous substance is designated, air quality modeling can be used to estimate a maximum allowable emission rate. For modeling purposes, disposal facilities can be considered as area sources with emissions occurring at ground level. In most cases it can be assumed that no plume rise will occur. Since the health effects being considered are thought to be related to long-term exposure, the modeling techniques recommended calculate annual average concentration estimates. The highest concentration caused by a ground-level source occurs near the source. However, it is not possible to estimate concentrations closer than 100 meters from a source using standard dispersion models. Therefore, the modeling for this regulation should focus on concentrations at 100 meters from the facility or, if the property line is greater than 100 meters from the facility, at the property line.

Two approaches are possible for estimating impacts of disposal facilities. The first approach is a screening technique, i.e., a simple approach suitable for making preliminary concentration estimates. The second approach is to use a refined model, i.e., a computer program for making reasonably accurate concentration estimates. It is not always possible to use the screening technique, in which case it is necessary to use the refined model at the outset. Also, if the screening technique suggests that the facility may have an unacceptable impact, the refined model should be used to estimate the impact more accurately.

The screening technique is based on treating the disposal facility as a virtual point source. Disposal facilities have their emissions initially spread over the area of the facility. The virtual source approach hypothesizes a point source located at an appropriate distance upwind such that the horizontal dispersion at the facility is equal to the facility width. The horizontal dispersion downwind of the facility can then be simulated as if all the facility emission were being emitted from the virtual point source.

The calculation of the impact of a disposal facility is simplified by using the virtual source approximation. Further simplification is possible by assuming that the facility is a ground-level source, assuming no atmospheric destruction or decay, and using one assumed meteorological situation. Starting, for example, with the equation underlying the Climatological Dispersion Model (2), the equation simplifies to:

$$\chi = \frac{16' \; 20}{2\pi L_v \sqrt{2\pi}\sigma_z u} \qquad (39)$$

where χ = net concentration (gr/m^3)

Q = emission rate (g/sec)

L_v = virtual downwind distance to receptor

σ_z = vertical dispersion coefficient (m) (given in Figure 1 as a function of downwind distance)

u = wind speed (m/sec)

In order to estimate the annual average concentration at a given receptor it is necessary to multiply this concentration by the frequency with which the given meteorological conditions occur. For the wind sector(s) in which the source impinges the receptor, refined models perform a summation of the concentration for each stability class and wind speed class times the frequency with which those conditions occur. The screening technique uses just one stability class and one wind speed to represent average conditions. The screening technique is limited to cases where the source emissions impinge the receptor in only one wind sector, i.e., the source lies entirely within one sector upwind. Since each sector is 22-1/2°, the source must be no more than $2L \tan(\frac{22\text{-}1/2°}{2})$. Thus, for a source to receptor distance (L) of 100 m, the screening technique should only be used if the source is less than 40 meters in width.

If the source is adequately small compared to the source-receptor distance, the screening technique can be used by using as a frequency factor the total frequency that the wind is in the sector of interest without regard to speed or stability class. The equation for calculating concentrations then becomes:

$$\chi = \left(\frac{16 \cdot 20}{2\pi L_v \sqrt{2\pi}\sigma_z u}\right) \cdot \phi \qquad (40)$$

where ϕ = frequency that wind blows from the sector of interest and other terms as defined above.

The following are recommendations for determining values for each of the parameters in the concentration equation:

χ - This is the net concentration resulting from uncontrolled emissions and is to be compared to the acceptable concentration. The concentration is proportional to the emission rate. Therefore, if the estimated concentration is a given factor higher than the acceptable concentration, then the acceptable emissions rate can be found by reducing the initially used emission rate by that factor.

Q - Earlier discussion in the document discusses the calculation of the emissions rate. Note that this is a total emissions rate for the entire area of the facility, gr./sec.

L_v - The determination of the downwind distance is complicated by the virtual source approach used in the screening technique. Let L be defined as the distance from the center of the facility to the receptor. As discussed above, L should be the greater of (1) the distance from facility center to property line, and (2) 100 meters. (Concentrations cannot be estimated less than 100 meters from a source.) The virtual point source approach also requires determining how far upwind a point souce would have to be located to have the same horizontal dispersion as is inherent in the area source. This distance from the virtual point to the center of a disposal facility (L') may be calculated here as:

$$L' = \frac{S}{2} \cot\left(\frac{22\text{-}1/2°}{2}\right) \qquad (41)$$

where S = the width of the facility perpendicular to the most frequent wind direction.- m.

The distance to be used in calculating concentrations is the total distance from virtual point to receptor, i.e., $L_v = L + L'$.

σ_z - Since D stability is by far the most frequently occurring stability class, σ_z should be taken from the curve for D stability as given in Figure 1 (taken from reference 19). The distance used to determine σ_z should be the distance from facility center to receptor (i.e., L , not L_v), because σ_z at the facility is assumed to be negligible.

u - Various references (e.g., the Climatic Atlas of the United states provide information on annual average wind speed. If these references or this data are not available, a default value of 5 m/sec may be used.

ϕ - The Climatic Atlas of U.S. also compiles the frequency that the wind blows from various directions for many U.S. cities. For this screening technique, ϕ should be set equal to the frequency of the most common of the standard 16 wind directions. If this information is not available, a default frequency of .15 may be used.

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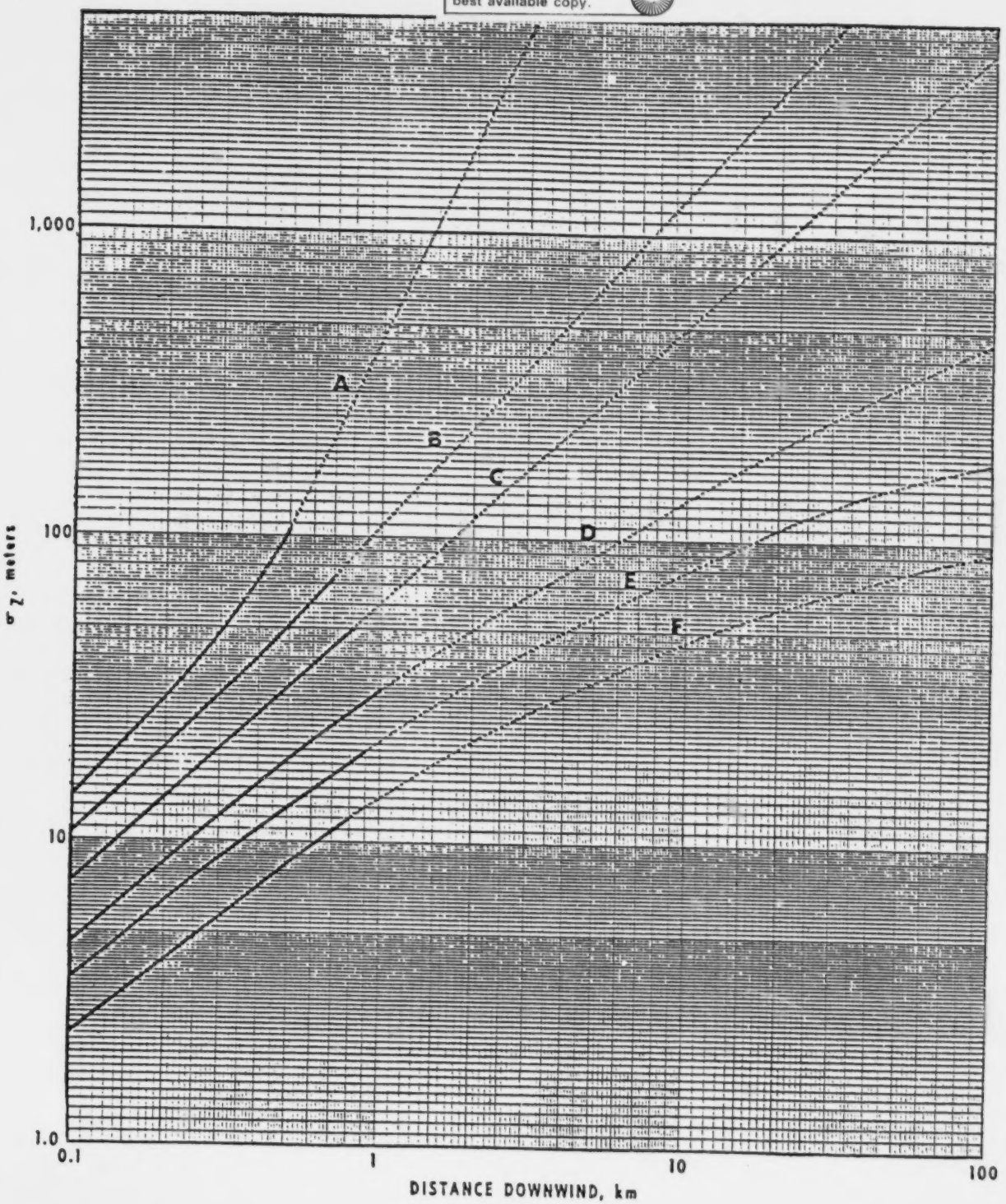

Figure 1. Vertical dispersion coefficient as a function of downwind distance from the source.

Estimates

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As discussed above, the screening technique is not always suitable for estimating the impact of a disposal facility. In particular, if the source width is greater than 40% of the distance from source center to receptor, the consideration of just one sector and the use of the virtual point source approach lead to increasingly less reliable concentration estimates.

If the screening technique is not suitable, or if the screening technique implies that unacceptable impacts may occur, the Climatological Dispersion Model should be used to obtain a more accurate estimate of concentrations. This model considers average emission rates, and the joint frequency distribution of wind speed and stability class for each of 16 wind directions. (This data is generally available from the National Climatic Center in Asheville, North Carolina.) This model also provides a more sophisticated integration of the impact of area sources. This model is a computerized model available on EPA's UNAMAP system. The model is described in Reference 1. Guidance on model inputs and other issues as given in the Guideline for Air Quality Model(20) should be followed in performing this modeling.

For acutely toxic pollutants assessment of short-term effects can be accomplished by using short-term air pollution dispersion analysis for ground level concentration effects. The prediction of the worst case conditions can be performed similarly.

IV. EVALUATION OF EXPOSURE CONCENTRATION

The subject of risk assessment will be covered more thoroughly in the permit writers guidance manual which EPA is planning to issue in the future. The presentation in this Chapter will focus on aspects of evaluation pertinent to arriving at acceptable ambient levels of hazardous substances. It is neither attempted to recommend a risk level nor to present an exhaustive list of chemicals exhibiting evidence of carcinogenesis or other health effects.

Harzardous materials volatilized from surface impoundments, landfills, and land treatment facilities will be dispersed into the atmosphere by wind and will impact the downwind population. The maximum allowable concentration represents the level that may result in incremental risk of human health over the short-term or long-term period at an assumed risk. For carcinogenic compounds for example, the long-term effect will be cancer risk over the lifetime. If one defines the unit risk for a carcinogenic compound (Ru) as lifetime risk if the concentration of a hazardous substance in the air is 1 $\mu gr/m^3$ and if this is breathed continuously for a lifetime, the maximum allowable concentration, C_{mi} ($\mu gr/m^3$), at a tolerable level of risk can be obtained by

$$C_{mi} = \text{risk}/Ru \qquad (42)$$

The unit risk for a number of hazardous compounds obtained from the EPA's Cancer Assessment Group is listed in Table 2 (12).

The background ambient concentration will indicate the present level of concentration at a locality, which becomes additive to the long-term or short-term effect on the downwind impact. In order to study the level of present ambient air risk for various toxic compounds, urban and rural ambient data for several compounds have been gathered. Table 3 summarizes the collected data. As one might have expected, the ambient air concentrations vary from location to location.

The Water Criteria Documents (6) make use of a risk range of 10^{-5} to 10^{-7} in presenting the exposure concentration levels of cacinogens.

Table 2. List of Chemicals Assessed
Weight of Carcinogenic Evidence

Chemical	Date	Excellent	Substantial	Suggestive	Inadequate Data	Unit Risk*
Acetaldehyde**	1/80			X		—
Acrolein**	2/80			X		—
Acrylonitrile	4/78	X				8.5×10^{-5}
Allyl Chloride*	9/79			X		9.9×10^{-7}
Arsenic	4/78	X				3.4×10^{-3}
Asbestos	6/78	X				—
Benzene	1/79	X				4.8×10^{-5}
Benzyl Chloride*	8/79				X	—
Beryllium**	12/79		X			2.7×10^{-1}
Cadmium*	5/76		X			2×10^{-3}
Chlorobenzene	9/79				X	—
Coke Ovens	3/78	X				—

*Changed from Dec. 18, 1979 memorandum from Joseph Padgett

**Added since Dec. 18, 1979 memorandum from Joseph Padgett

List of Chemicals Assessed
Weight of Carcinogenic Evidence

Chemical	Date	Excellent	Substantial	Suggestive	Inadequate Data	Unit Risk
o-Cresol	6/79				X	——
m-Cresol	6/79				X	——
p-Cresol	6/79				X	——
o-Dichlorobenzene	9/79				X	——
p-Dichlorobenzene	9/79			X		——
Diethyl-nitrosamine (DEN)**	12/79		X			7.2×10^{-2}
Dimethyl-nitrosamine (DMN)**	12/79		X			0.29×10^{-2}
Ethylene Dibromide	4/78		X			5.9×10^{-4}
Ethylene Dichloride	6/78		X			1.2×10^{-5}
Ethylene Oxide*	10/79		X			1.2×10^{-4}
Formaldehyde	11/79		X			3.4×10^{-5}
Maleic Anhydride*	2/79				X	——

*Changed from Dec. 18, 1979 memorandum from Joseph Padgett

**Added since Dec. 18, 1979 memorandum from Joseph Padgett

List of Chemicals Assessed
Weight of Carcinogenic Evidence

Chemical	Date	Excellent	Substantial	Suggestive	Inadequate Data	Unit Risk
Manganese	8/79			X		4.8×10^{-4}
Methyl Chloroform	1/79			X		—
Methylene Chloride	1/79			X		—
Methyl Iodide	9/79			X		—
Nickel**	12/79	X				1.8×10^{-3}
Nitrobenzene	6/79				X	—
N-nitroso-N-ethylurea (NEU)**	12/79		X			$.65 \times 10^{-2}$
N-nitroso N-methylurea (NRU)**	12/79		X			3.5×10^{-2}
Perchloroethylene	4/78		X			7.6×10^{-6}
Phosgene	8/79				X	—
Polycyclic Organic Matter	7/78	X				—
Propylene Oxide	9/79			X		—

*Changed from Dec. 18, 1979 memorandum from Joseph Padgett

18, 1979 memorandum from Joseph Padgett

List of Chemicals Assessed
Weight of Carcinogenic Evidence

Chemical	Date	Excellent	Substantial	Suggestive	Inadequate Date	Unit Risk
Toluene	8/79				X	——
Trichloroethylene	8/78		X			4.2×10^{-6}
Vinyl Chloride	8/78	X				4.1×10^{-6}
Vinylidene Chloride*	5/78		X			3.0×10^{-5}
o-Xylene	9/79				X	——
m-Xylene	9/79				X	——
p-Xylene	9/79				X	——

*Changed from Dec. 18, 1979 memorandum from Joseph Padgett

**Added since Dec. 18, 1979 memorandum from Joseph Padgett

POM - It should be emphasized that POM represents a mixture of organic compounds. There is substantial evidence that some components of POM particularly from combustion processes are associated with induction of human cancer. Special attention should be given to POM emission because not all the components have evidence for its carcinogenic action. So the source and composition is important in characterizing the specific POM emission.

Beryllium - The risk unit is very high and may be revised when final data are available from the Mancuso study.

Table 3. Ambient Air Concentrations of Probable Carcinogens*

Chemical	Los Angeles Calif. Ranges	Los Angeles Calif. Av.	New York N. Y. Ranges	New York N. Y. Av.	Azusa Calif. Av.	Bayonne N. J. Ranges	Near Gas Station Ranges	Urban Ranges	Urban Av.	Rural or Background Av.
Acetaldehyde	highest 13.1(6)	7.9(6)								
Acrolein										
Acrylonitrile										
Allyl Chloride										
Arsenic								(1000) ~ (83000)(6)	(3000)(6)	(400)(6)
Asbestos			(0.003) ~ (0.065)(6)	(0.015)(6)						
Benzene	57(1)	15(1)					300 ~ 2400(6)			0.017(6)
Benzyl Chloride										
Beryllium								(0.001) ~ (0.008)(6)	(0.0015)(6)	(0.0001 ~
Cadmium			(0.006) ~ (0.007)(8)					(0.001) ~ (0.3)(8)	(0.03)(8)	0 ~ (0.0001)(8)
Chlorobenzene										
Coke Ovens										

* Concentrations in ppb; ( ) in $\mu gr/m^3$. Superscript refers to the reference cited.

Chemical	Urban		Rural or Background
	Ranges	Av.	Av.
o-Cresol			
m-Cresol			
p-Cresol			
o-Dichlorobenzene			
p-Dichlorobenzene			
Diethyl-nitrosamine (DEN)		~0(6)	
Dimethyl-nitrosamine (DMN)		(0.1) ~(36)	(0.001) ~(0.04)
Ethylene Dibromide			
Ethylene Dichloride			
Ethylene Oxide			
Formaldehyde			
Maleic Anhydride			

Chemical	Los Angeles Calif. Ranges	Los Angeles Calif. Av.	New York N. Y. Ranges	New York N. Y. Av.	Azusa Calif Av.	Bayonne N. J. Near Gas Station	Urban Ranges	Urban Av.	Rural or Background Av.
Manganese									
Methyl Chloroform									
Methylene Chloride	0.6 ~12	3.8					0.01 ~12	0.05	0.035
Methyl Iodide									
Nickel								(0.009)	(0.002)
Nitrobenzene									
N-nitroso-N-ethylurea (NEU)									
N-nitroso N-methylurea (NRU)									
Perchloroethylene							0.001 ~10		0.009
Phosgene									
Polycyclic Organic Matter									
Propylene Oxide									

	Los Angeles Calif.		New York N. Y.		Azusa Calif	Bayonne N. J.	Near Gas Station	Urban		Rural or Background
	Ranges	Av.	Ranges	Av.	Av.	Range		Range	Av.	Av.
Chemical										
Toluene	~125(1)	37(1)			14(1)					
Trichloroethylene										
Vinyl Chloride										
Vinylidene Chloride										
o-Xylene	~33(1)	8(1)			3(1)					
m-Xylene	~61(1)	16(1)			5.5(1)					
p-Xylene	~25(1)	6(1)			2(1)					
Hexachlorobenzene										
Chloroform						(0.49)~ (73)(6)				(0.49)(6)
PAH								(0.0436)(6)		
Toxaphene								0 ~ (1.54)(6)	(0.02)(6)	(0.00053)(
TCDD										
Carbon Tet.						0.12 ~ 18.6				0.13

Table 4. Comparison of Ambient Air Concentrations and Maximum Allowable Concentrations @ 10^{-5} Ris

Chemical	Unit Risk	Concentration @ 10^{-5} Risk $\mu gr/m^3$	Concentration @ 10^{-5} Risk ppb	Ambient Air Conc.(ppb) Urban Av.	Ambient Air Conc.(ppb) Rural or Background
Acetaldehyde					
Acrolein				7.9	
Acrylonitrile	$8.5x10^{-5}$	0.1176	0.054		
Allyl Chloride	$9.9x10^{-7}$	10.1	3.23		
Arsenic	$3.4x10^{-3}$	$2.94x10^{-3}$	---	(3000)	(400)
Asbestos					
Benzene	$4.8x10^{-5}$	0.208	0.065	3 - 15	0.017
Benzyl Chloride					
Beryllium	$2.7x10^{-1}$	$3.7x10^{-5}$	---	(0.0015)	$(1.3x10^{-4})$
Cadmium	$2x10^{-3}$	$5x10^{-3}$	---	(0.001) ~(0.03)	0 ~ (0.0001)
Chlorobenzene					
Coke Ovens					

Concentration in (, , 3

Chemical	Unit Risk	Concentration @ 10^{-5} Risk		Ambient Air Concentration	
		$\mu gr/m^3$	ppb	Urban Av.	Rural or Background
o-Cresol					
m-Cresol					
p-Cresol					
o-Dichlorobenzene					
p-Dichlorobenzene					
Diethyl-nitrosamine (DEN)	7.2×10^{-2}	1.39×10^{-4}	3.3×10^{-5}	~0	
Dimethyl-nitrosamine (DMN)	0.29×10^{-2}	3.45×10^{-3}	1.14×10^{-3}	(0.1)~ (36)	1×10^{-3}
Ethylene Dibromide	5.9×10^{-4}	1.7×10^{-2}	2.2×10^{-3}		
Ethylene Dichloride	1.2×10^{-5}	0.83	0.206		
Ethylene Oxide	1.2×10^{-4}	8.3×10^{-2}	0.046		
Formaldehyde	3.4×10^{-5}	0.294	0.24		
Maleic Anhydride					

Chemical	Unit Risk	Concentration @ 10^{-5} Risk $\mu gr/m^3$	ppb	Ambient Air Concentration Urban Av.	Rural or Backgrour
Manganese		$2.08x10^{-2}$			
Methyl Chloroform					
Methylene Chloride				0.05	0.035
Methyl Iodide					
Nickel	$1.8x10^{-3}$	$5.56x10^{-3}$		$(9x10^{-3})$	$(2x10^{-3})$
Nitrobenzene					
N-nitroso-N-ethylurea (NEU)	$0.65x10^{-2}$	$1.54x10^{-3}$	$3.2x10^{-4}$		
N-nitroso N-methylurea (NRU)	$3.5x10^{-2}$	$2.86x10^{-4}$	$6.78x10^{-5}$		
Perchloroethylene	$7.6x10^{-6}$	1.32	0.194	0.001 ~10	0.009
Phosgene					
Polycyclic Organic Matter					
Propylene Oxide					

Chemical	Unit Risk	Concentration @ 10^{-5} Risk		Ambient Air Concentration	
		$\mu gr/m^3$	ppb	Urban Av.	Rural or Background
Toluene				10	
Trichloroethylene	4.2×10^{-6}	2.38	0.44		
Vinyl Chloride	4.1×10^{-6}	2.44	0.954		
Vinylidene Chloride	3.0×10^{-5}	0.33	0.082		
o-Xylene				5	
m-Xylene				10	
p-Xylene				4	
Hexachlorobenzene	5.71×10^{-4} *	1.75×10^{-2}	0.0015		
Chloroform	6.29×10^{-5} *	0.159	0.033	0.1 - 15	0.1
PAH	1.7×10^{-3} *	5.89×10^{-3}	7.2×10^{-4}	5.3×10^{-3}	
Toxaphene	9.43×10^{-4} *	1.06×10^{-2}	6.26×10^{-4}	1.18×10^{-3}	1.28×10^{-6}
TCDD		1.27×10^{-6}	1.1×10^{-7}		
Carbon Tet.	2.4×10^{-5} *	0.417	0.066	0.12 - 18.6	0.13
PCB	1.35×10^{-3} **	0.0075			

* From water quality criteria documents.

** Calculated from potency slope(4.34 1/mg/kg day) obtained from ingestion study.

Table 4 is a comparison of the ambient air data with the maximum allowable concentration calculated at 10^{-5} risk. The third and fourth columns in the table represent the maximum allowable concentrations at 10^{-5} risk in $\mu gr/m^3$ and ppb respectively. The ambient air concentration values which are considered "representative" for background are chosen and tabulated in Columns 5 and 6 for the purpose of comparison. It can be seen that the present ambient levels of some compounds are already too high to meet the 10^{-5} risk value. In fact, in certain urban areas, the ambient air levels exceed 10^{-5} risk at present. The ambient air concentrations higher than those in Table 3 are reported in Reference (28) for several metropolitan areas in the State of California.

In an area with a higher background concentration, the emission rate allowable for a disposal facility should be comparatively less. In view of the fact that the present ambient air concentrations are mostly higher than the level at 10^{-5} risk, it may not be possible to achieve the maximum allowable concentration calculated by Equation (42) at that risk. The case-by-case evaluation will determine whether or not the facility will contribute significantly to degradation of present ambient levels so as to require reduction or elimination of hazardous emissions. The permit evaluation will consider risk assessment in consistency with other criteria goals.

Table 2 does not attempt to present exhaustively all carcinogenic compounds, but is merely a collection of data that the EPA's CAG has compiled at the time this report is completed. It is not meant to limit control and risk assessment of hazardous air emissions only to those compounds in the list. The compounds which are missing from the list or the data of which are inadequate or incomplete will be added to the list

as more data become available. If the results of a health effect study on another compound become available from some other source, such information could be used as a basis of evaluating the allowable exposure concentrations.

Also other effects on human health due to exposure to high ambient air concentrations of chemicals should not be neglected during the evaluation process. These effects include acute toxicity, responses to central nervous system, teratogenicity, mutagenicity, bioaccumulation, radioactivity, nephrotoxicity, hepatotoxicity, phytotoxicity, toxicity to aquatic species, photochemical reactivity, etc. The compilation of data concerning these effects is not available at this time. An example presented later will address the tecknique of evaluating the health effect potential based on other criteria goals.

In the case of emissions of total hydrocarbons, a caution should be exercised in evaluating the impact of a facility located in the area where the ambient air quality of photochemical oxidants is not presently acceptable. Since most of hydrocarbons (except methane) participate in the formation of photochemical smog sooner or later depending upon its reaction rates, the prevention of further degradation of the ambient air quality of photochemical oxidants can be achieved by removal of volatile hydrocarbons to the extent possible.

Table 5 shows the upwind and downwind concentrations of several compounds in the ambient air around land disposal facilities (29). The organic species were collected on Tenax adsorbent and analyzed by GC/FID after identifying with GC/MS. Trace metals were collected on high-volume filters and analyzed from the collected particulates.

TABLE 5 CONCENTRATIONS OF SELECTED HAZARDOUS ORGANIC VAPORS FOUND IN THE AMBIENT AIR AT HAZARDOUS WASTE FACILITIES

Facility Code No.	Background Type ①	Ambient Air Concentrations, ppb															
		n-Hexane		Benzene		n-Heptane		Toluene		n-Octane		Ethyl Benzene		Xylenes		Dichloro-Benzene		Naphthalene	
		Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind
13	R, I	15.0	11.0	4.0	5.0	42.0	2.0	58.0	60.0	6.7	2.2	4.9	11.0	10.0	32.0	0.0	1.6	0.0	0.8
14	R, I	3.4	10.0	8.4	83.0	3.0	15.0	22.0	30.0	2.3	3.8	3.0	8.8	10.0	16.0	0.0	0.0	0.2	0.0
15	R	7.4	20.0	6.1	240.0	4.4	100.0	26.0	170.0	1.4	25.0	3.4	64.0	15.0	240.0	0.3	26.0	0.5	22.0
16	R	14.0	42.0	11.0	44.0	12.0	36.0	106.0	150.0	5.0	31.0	21.0	24.0	94.0	100.0	3.0	3.0	0.0	
17	U	24.0	98.0	28.0	84.0	27.0	97.0	150.0	950.0	20.0	46.0	28.0	37.0	79.0	140.0	3.0	6.6	3.0	8.0
18	U	15.0	42.0	10.0	57.0	11.0	62.0	8.5	30.0	8.0	38.0	16.0	56.0	54.0	270.0	0.8	3.7	0.4	4.0

① Background Type: R = Rural, I = Industrial, U = Urban

TABLE 5 PARTICULATE TRACE METALS IN AMBIENT AIR AT HAZARDOUS WASTE FACILITIES

Facility Code No.	Back-Ground Type①	Trace Metal Concentration, µg/m³															
		Cadmium		Chromium		Cobalt		Copper		Iron		Lead		Nickel		Zinc	
		up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind
01	U	BDL②	BDL	0.14	0.18	BDL	BDL	0.12	0.16	3.2	5.9	0.51	0.62	BDL	0.03	0.08	0.33
04	R	BDL	BDL	.11	.12	BDL	BDL	.01	.15	.40	1.69	.06	.90	BDL	BDL	BDL	.08
05	R	BDL	BDL	BDL	BDL	BDL	BDL	BDL	.04	.36	10.7	.04	.47	.04	.05	BDL	BDL
06	R	BDL	BDL	.07	.17	.04	.04	.05	.13	4.0	30.9	.45	.80	.03	.14	.02	.46
07	U	BDL	BDL	BDL	.45	.07	.13	.06	.84	10.5	71.4	.90	2.83	.04	.35	.23	2.45
08	R	BDL	BDL	BDL	BDL	.07	.05	.05	.03	1.0	2.8	.32	.34	.05	.02	BDL	.62
09	R	BDL	BDL	BDL	BDL	BDL	BDL	.16	.20	.47	.29	.09	.09	BDL	BDL	BDL	.11
10	U	BDL	BDL	BDL	.04	BDL	BDL	.27	.27	6.0	5.9	.67	.54	BDL	BDL	.21	.46
11	U	BDL	BDL	.03	BDL	BDL	BDL	.12	.08	3.9	4.6	.35	.38	BDL	BDL	.43	.42
12	U	BDL	BDL	BDL	BDL	.01	.02	.13	.09	5.5	5.6	.41	.54	BDL	BDL	.46	.44
13	R,I	BDL	BDL	BDL	BDL	BDL	BDL	.03	.06	.53	2.7	BDL	.13	BDL	.02	.05	.10
14	R,I	BDL	BDL	BDL	BDL	BDL	BDL	.12	.02	.44	.54	.06	.13	BDL	BDL	.08	.16
15	R	BDL	BDL	BDL	BDL	BDL	BDL	.05	.01	3.4	10.2	.18	.28	.02	.12	.06	.07
16	R	BDL	.03	BDL	BDL	BDL	BDL	.02	.03	.70	.87	.02	.06	.01	BDL	.02	.04
17	U	.03	.04	.02	.08	BDL	BDL	.28	.17	5.2	21.1	.91	1.23	.05	.09	.28	.70
18	U	BDL	.03	BDL	.12	BDL	BDL	.11	.19	3.9	28.8	.42	2.19	.02	.11	.03	1.53
DL③, µg/m³		.02		.01		.01		.01		.02		.01		.02		.01	

① Background type: R = Rural, U = Urban, I = Industrial

② BDL = Below detection limit

③ DL = Detection Limit

V. CONTROL TECHNOLOGIES

Removal of volatiles from the waste prior to disposal will reduce their air emissions. Some suggest the use of wind barriers to slow down emission rates from surface impoundments. The techniques of removing volatile organic compounds from wastewaters have been extensively reviewed previously (9), (10).

Steam stripping is one of the control alternatives for removal of volatiles from wastewater prior to surface impoundment. For hydrocarbon mixtures, control alternatives would be recycle or recovery of volatiles by conventional distillation processes, or disposal by incineration. Use of adequate cover material for landfills and adequate depth of subsurface injection for land treatment may provide some or considerable reduction in air emissions.

Hazardous wastes landfilled with sanitary wastes are subject to considerable volatilization as a result of decomposition of waste material. Extraction of decomposition gas from sanitary landfills has been practiced by means of a collection system which consists of a series of gas wells operating under vacuum. The evaluation of an emission potential of such a landfill will require knowledge on the emission rate from the landfill, and the gas collection rate.

VI. EXAMPLE CALCULATIONS

1. Estimation of Emission Rates from Surface Impoundments

A wastewater being treated in a POTW was analyzed for its toxic compounds. The following data was obtained

Compound	Concentration (mg/L)
Benzene	20
Acrylonitrile	3
Chloroform	10
Perchloroethylene	1

The POTW has a surface area of 0.25 acre, about 10% of which is estimated to be the effective zone of turbulence. Estimate the emission rates from the surface impoundment.

The gas and liquid phase mass transfer coefficients for convective and turbulent zones can be calculated using Equations (10) - (13). Specific examples for benzene (MW=78.1) at 25°C is given below.

i) Convective zone

a) Liquid phase

$$k_{L,i} = \left(\frac{32}{78.1}\right)^{0.5} \left(\frac{273 + 25}{298}\right) 2.4 \times 10^{-5}$$

$$= 1.54 \times 10^{-5} \ \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

b) Gas phase

$$k_{g,i} = \left(\frac{18}{78.1}\right)^{0.335} (1)^{1.005} \ 2.7 \times 10^{-5} = 1.65 \times 10^{-5} \ \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

ii) Turbulent(or Aerated) zone

a) Liquid phase

$$k_{L,i} = \left(\frac{32}{78.1}\right)^{0.25} \frac{1.024^{25-20}}{1.024^{5}} (1)^{0.5} \quad 0.12 = 0.096 \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

b) Gas phase

$$k_{g,i} = \left(\frac{18}{78.1}\right)^{0.25} (1)^{0.92} \quad 4.6 \times 10^{-4} = 3.19 \times 10^{-4} \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

We need to know the value of vapor-liquid equilibrium constant, K, to combine the gas-phase and liquid-phase mass transfer coefficients. From the example given in the appendix, one can get K = 308 for benzene at 25°C. The overall liquid phase mass transfer coefficients in the convective ($(K_L)_C$) and turbulent ($(K_L)_T$) zones are calculated using Equation (2)

$$\frac{1}{(K_L)_C} = \frac{1}{1.54 \times 10^{-5}} + \frac{1}{308 \times 1.65 \times 10^{-5}} = 6.51 \times 10^{4}$$

$$(K_L)_C = 1.54 \times 10^{-5} \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

$$\frac{1}{(K_L)_T} = \frac{1}{0.096} + \frac{1}{308 \times 3.19 \times 10^{-4}} = 20.6$$

$$(K_L)_T = 0.049 \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

Use of Equation (14) yields the area-averaged overall mass transfer coefficients,

$$K_L = 1.54 \times 10^{-5} (0.9) + 0.049 (0.1) = 0.00491 \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

Note: The overall liquid phase mass transfer coefficient given in gr-mol/cm^2·sec can be converted to the unit of cm/sec, or 1/sec as follows.

density of the wastewater = 1 gr/cm^3

$$K_L \text{ (in cm/sec)} = \frac{0.00491 \times 78.1}{1} = 0.38 \text{ cm/sec}$$

or if the depth of the surface impoundment is 304.8 cm(10 ft),

$$K_L \text{ (in 1/sec)} = \frac{0.38}{304.8} = 1.25 \times 10^{-3} \text{ 1/sec}$$

The concentration of benzene in mg/L can be converted to mole fraction:

$$x_i = \frac{20}{10^3} \times \frac{1}{10^3} \times \frac{1/78.1}{1/18}$$

$$= \frac{20}{10^6} \frac{18}{78.1} = 4.61 \times 10^{-6}$$

Equation (3) is used to calculate the emission rate for benzene

$$Q_i = 78.1\ (0.00491)\ (0.25 \times 4047 \times 10^4)\ (4.61 \times 10^{-6})$$

$$= 17.9 \text{ gr/sec}$$

Similar calculations will yield the emission rates for other toxic components.

2. Estimation of Emission Rates from Landfills

i) Hazardous waste is to be landfilled. The proposed 1/2 acre landfill will be covered by a soil layer of 30 cm above the hazardous waste section. The laboratory tests on soil show an average yearly porosity of 0.16. The vapor in equilibrium with the waste was analyzed

for the compounds among the list of carcinogenic evidence using the head space method. The results of the analysis are:

Compound	Concentration in Vapor Space (% by volume)	Equilibrium PARTIAL PRESSURE (mmHg)
Benzene	0.96	7.3
Trichloroethylene	0.149	1.13
Ethylene Dichloride	0.916	6.96

Estimate the emission rates from the landfill.

Since the air phase resistance is small, Equation (16) can be rewritten as

$$q_i = \frac{\epsilon \cdot D_i}{h \cdot \tau} C_i^*$$

The diffusion coefficient of benzene at 25°C is estimated using Equation (20)

$$D_i = 1.5 \times 10^{-4} \left(\frac{1}{78.1} \right)^{0.5} (273 + 25)^{1.5} = 0.088 \text{ cm}^2/\text{sec}$$

The concentration of benzene in the vapor in equilibrium with the waste is calculated from Equation (21)

$$C_i^* = \frac{7.3 \ (78.1)}{62363 \ (298)} = 3.07 \times 10^{-5} \text{ gr/cm}^3$$

Hence

$$Q_i = \frac{0.16 \ (0.088)}{30 \ (1.73)} (3.07 \times 10^{-5}) 0.5 \ (4047 \times 10^4) = 0.17 \text{ gr/sec}$$

Similar calculations will give the emission rates for trichloroethylene and ethylene dichloride.

Q_i for trichloroethylene = 0.034 gr/sec

Q_i for ethylene dichloride = 0.18 gr/sec

ii) The proposed landfill in example i above is redesigned to employ a soil cover with thickness of 60 cm. Polyethylene film (thickness 0.03 cm) will be placed between the waste and the cover. Analyses were performed on the waste , instead of its equilibrium vapor, to determine the composition. The results of the analysis are:

Benzene 3 % by weight

Trichloroethylene 1 % by wt.

Ethylene dichloride 4 % by wt.

Sp. Gr. of the waste : 0.9 gr/cm^3

The soil tests showed an annual average moisture content of 19 % at a bulk density of 1.15gr/cm^3. Evaluate the landfill as before.

The polyethylene film can be converted to equilibrium soil thickness. The use of Equation (16) to obtain the thickness of soil corresponding to bulk density of 1.19 gr/cm^3 and a soil moisture content of 20 % gives

$$h_{eq} = 134.6\ h_f$$

$$= 134.6\ (0.03) = 4\ cm$$

The air-filled porosity and total porosity of the soil are

$$P_a = 1 - \frac{1.15}{2.65} - 0.19(1.15) = 0.348$$

$$P_T = 1 - \frac{1.15}{2.65} = 0.566$$

$$P_a^{10/3} / P_T^2 = 0.348^{10/3}/0.566^2 = 0.0925$$

The partial pressure P_i^* of each component i in equilibrium with

the waste can be estimated by

$$p_i^* = K_i P x_i$$

where K_i is the vapor liquid equilibrium constant (It can be obtained using the method shown in the appendix ; $K_i = \gamma_i P_i^o/P$), γ_i is the activity coefficient of component i(assumed to be 1 in hydrocarbon mixtures), P_i^o is the vapor pressure of component i, mmHg, P is the total pressure, 760 mmHg, x_i is the mole fraction of component i in the waste.

1) benzene (3 % by wt.)

$$x_i = \frac{3/78.1}{100/200} = 0.0768 \text{ mole fr.}$$

$$p_i^* = 0.0768\ (95) = 7.3 \text{ mmHg}$$

Similarly

2) trichloroethylene

$$p_i^* = 1.13 \text{ mmHg}$$

3) ethylene dichloride

$$p_i^* = 7 \text{ mmHg}$$

Hence the quilibrium vapor phase concentrations can be computed as in Example i:

C_i^* for benzene = 3.07×10^{-5} gr/cm^3

C_i^* for trichloroethylene = 8×10^{-6} gr/cm^3

C_i^* for ethylene dichloride = 3.73×10^{-5} gr/cm^3

Use of Equation (28) yields the estimated emission rates

$$Q_i \text{ for benzene} = 0.088 \left[\frac{1}{\frac{60}{0.0925} + 1962.8(0.03)} \right] (3.07\times10^{-5}) 0.5 (4047\times10^{4})$$

$$= 0.077 \text{ gr/sec}$$

Q_i for trichloroethylene = 0.016 gr/sec

Q_i for ethylene dichloride = 0.084 gr/sec

iii) The wastes in Examples i and ii are to be landfilled after mixing with municipal garbage. Estimate the emission rates for each case.

a) Example i with gas generation

The gas generated as result of decomposition of the garbage will contribute to additional release of hazardous air pollutants. The emission rate will be estimated from Equation (22) at an average velocity of generated gas at 1.63×10^{-3} cm/sec in the landfill (17). To use Equation (22) the concentration at the interface, C_{io}, must be known. An expression for it can be obtained by equating Equation (22) and Equation (23), or

$$C_{io} = \frac{C_i^* \exp\left(\frac{h \cdot \bar{V} \cdot \tau}{D_i \cdot \epsilon}\right)}{1 + \frac{k_{g,i}(2.44 \times 10^4)}{\bar{V}} \left(\exp\left(\frac{h \cdot \bar{V} \cdot \tau}{D_i \epsilon}\right) - 1\right)} \qquad (43)$$

The gas-phase mass transfer coefficients required in Equation (43) are obtained from the relationship given by Equation (11),

$$k_{g,i} \text{ for benzene} = \left(\frac{MW_{H_2O}}{MW_i}\right)^{0.335} \left(\frac{273 + 25}{298}\right)^{1.005} k_{g,H_2O}$$

$$= \left(\frac{18}{78.1}\right)^{0.335} 2.7 \times 10^{-5} \; 1.65 \times 10^{-5} \; \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

Similarly,

$k_{g,i}$ for trichloroethylene = 1.4×10^{-5} gr-mol/cm^2·sec

$k_{g,i}$ for ethylene dichloride = 1.53×10^{-5} gr-mol/cm^2·sec

The interface concentrations are

1) benzene

$$\frac{h \cdot \bar{v} \cdot \gamma}{D_i \cdot \epsilon} = \frac{30(1.6\times10^{-3})(1.73)}{0.088(0.16)} = 6.01$$

$$C_{io} = \frac{3.07\times10^{-5} \; e^{6.01}}{1 + \frac{1.65\times10^{-5}(2.44\times10^{4})}{1.63\times10^{-3}}\left(e^{6.01} - 1\right)}$$

$$= 1.25 \times 10^{-7} \text{ gr/cm}^3$$

2) trichloroethylene

$D_i = 1.5\times10^{-4}(1/131.4)^{0.5} \; 298^{1.5} = 0.067$

$C_{io} = 3.24\times10^{-8}$ gr/cm^3

3) ethylene dichloride

$D_i = 0.078$

$C_{io} = 1.63\times10^{-7}$ gr/cm^3

Hence the emission rates estimated from Equation (22) are

1) benzene

$$Q_i = \left[1.63\times10^{-3} \frac{3.07\times10^{-5} - 1.25\times10^{-7}}{e^{6.01} - 1} + 1.63\times10^{-3}(3.07\times10^{-5})\right](0.5)$$

$$\times (4047\times10^{4}) = 1.02 \text{ gr/sec}$$

2) trichloroethylene

Q_i = 0.26 gr/sec

3) ethylene dichloride

Q_i = 1.22 gr/sec

b) Example ii with gas generation

Equation (29) will be used to estimate the emission rates. As seen above, $C_{io} << C_i^*$. Hence C_{io} can be neglected in Equation (29). The emission rate for benzene is

$$Q_i = \left[1.63\times10^{-3} \frac{3.07 \times 10^{-5}}{\exp\left[\frac{1.63\times10^{-3}}{0.088}\left(\frac{60}{0.0925} + 1962.8(0.03)\right)\right] - 1} + 1.63\times10^{-3}(3.07\times10^{-5}) \right] (0.5)(4047\times10^{4}) = 1.01 \text{ gr/sec}$$

Similarly,

Q_i for trichloroethylene = 0.26 gr/sec

Q_i for ethylene dichloride = 1.22 gr/sec.

3. Estimation of Emission Rates from Land Treatment Facilities.

An oily waste is treated in a one acre landfarm by subsurface injection at an application rate of 1.5 #/ft^2. The depth of injection is 5' (12.7 cm). The waste analysis shows the presence of benzene in the oil at a level of 1500 ppm by weight. The porosity of the soil in the cultivation layer is determined to be 0.35 by test. Estimate the average emission rates. Other pertinent information:

Average MW of the waste: 200

Sp gr. of the waste : 0.9 gr/cm^3

Cultivation layer soil bulk density: 0.8 gr/cm^3

The use of Equation (30) requires the concentration of benzene on the vapor side of the oil-vapor interface, which can be calculated from Equation (31).

The initial concentration of benzene in the oil

$$C_{iwo} = \frac{1500}{10^6/0.9} = 1.35 \times 10^{-3} \text{ gr/cm}^3$$

The application rate = 1.5 #/ft^2, or

$$\frac{M_T}{A} = 1.5 \times \frac{454}{30.48^2} = 0.733 \text{ gr/cm}^2$$

The total depth of penetration

$$h_p = h_s + \text{depth of penetration} = 12.7 + 12.7 = 25.4 \text{ cm}$$

The mass fraction oil in the film form (Equation (38))

$$w_f = \frac{0.5}{h_p \bar{\rho}_B} \left(\frac{M_T}{A} \right) = \frac{0.5}{(25.4)(0.8)} (0.733)$$

$$= 0.018$$

From Equation (34), the oil film thickness on soil is (use d_p = 0.005 cm)

$$z_o = \frac{0.005(2.65)(0.018)}{6(0.9)} = 0.000044 \text{ cm}$$

From Equation (35) the diffusion path length for the lump is

$$z_o = 0.005/2 = 0.0025 \text{ cm}$$

The vapor pressure of benzene at 25°C is 95 mmHg. If the activity coefficient of benzene in oil is assumed to be unity for a total pressure of 760 mmHg, the vapor liquid equilibrium constant K = 0.125 (See Eq.(A-5) in the appendix). Using Equation (A-8) in the appendix, one gets

$$H_c = \frac{0.125}{2.44\text{x}10^{4}} \frac{200}{0.9} = 1.14\text{x}10^{-3}$$

Also

D_{wi} for benzene in oil = $1\text{x}10^{-7}$ cm^2/sec ($D_{wi} \propto \frac{1}{\mu}$; $D_{wi}=10^{-5}$ @ μ=1cp)

$D_{ei} = D_i \epsilon^{4/3}$ (recommended by Thibodeaux(26))

$0.088\text{x}(0.35)^{4/3} = 0.022$ cm^2/sec

a_s for film (Equation (36)) = $6/0.005 = 1200$ cm^2/cm^3

a_s for lump (Equation (37)) = $2.7/0.005 = 540$ cm^2/cm^3

Substitution of these values into Equation (31) yields

$$C_{ig} \text{ for film} = \left[\frac{1.14\text{x}10^{-3}}{1 + 1.14\text{x}10^{-3} \frac{6(0.022)(0.000044)}{1\text{x}10^{-5}(1200)(645)}} \right] (1.35\text{x}10^{-3})$$

$$= 1.54\text{x}10^{-6} \text{ gr/cm}^3$$

where $h_p^2 + h_p h_s - 2 h_s^2 = 25.4^2 + (25.4)(12.7) - 2(12.7)^2 = 645 \text{ cm}^2$

$$C_{ig} \text{ for lump} = \left[\frac{1.14 \times 10^{-3}}{1 + 1.14 \times 10^{-3} \dfrac{6(0.022)(0.0025)}{1 \times 10^{-7}(540)(645)}} \right] (1.35 \times 10^{-3})$$

$$= 1.54 \times 10^{-6} \text{ gr/cm}^3$$

$\frac{m_{io}}{A}$ (wt. of benzene applied per unit area of landfarm)

$$= 0.733 \times \frac{1500}{10^6} = 1.1 \times 10^{-3} \text{ gr/cm}^3$$

The dry-out time is calculated using Equation (33)

$$t_d \text{ for film} = \frac{25.4 + 12.7}{2(0.022)(1.54 \times 10^{-6})} (1.1 \times 10^{-3})(0.5) = 3.1 \times 10^5 \text{ sec}$$

(3.6 days)

$$t_d \text{ for oil} = \frac{38.1}{2(0.022)(1.54 \times 10^{-6})} (1.1 \times 10^{-3})(0.5) = 3.1 \times 10^5 \text{ sec}$$

In this case the dry-out times for both film and oil lump are the same, From Equation (30) the average emission rate during the period of the dry-out time is

$$\bar{Q}_i \text{ for film layer} = \frac{2(0.022)\ (1.54 \times 10^{-6})(4047 \times 10^4)}{\left[12.7^2 + \dfrac{2(0.022)(3.1 \times 10^5)(12.7)(1.54 \times 10^{-6})}{1.1 \times 10^{-3}(0.5)} \right]^{1/2}}$$

$$= 0.11 \text{ gr/sec}$$

$\bar{Q}_i$ for oil layer = 0.11 gr/sec

The average emission rate is

$$0.11 + 0.11 = 0.22 \text{ gr/sec}$$

4. Dispersion Modeling-Screening Technique

A disposal facility (1/2 acre) is emitting volatile hazardous chemicals at the following rates:

Compound	Emission Rate(gr/sec)
benzene	0.17
trichloroethylene	0.034
ethylene dichloride	0.18

Evaluate the impact of the facility on ambient air quality.

In order to utilize the screening technique for estimating the impact, the following data are obtained from the permit applicant:

Distance from the facility to the downwind public: L=1000 m

Frequency that wind blows from the sector of interest: $\phi = 0.25$

Average annual temperature: $25^{\circ}C$

Stability Class: D

Annual average wind speed: 5 m/sec

At L = 1000 m & D stability, σ_z = 32 m.

Distance from virtual point to the disposal facility (Equation (41))

$$L' = \frac{(0.5 \times 4047 \times 10^4)^{0.5}}{2} \cot\left(\frac{22.5}{2}\right) = 11300 \text{ cm } (113 \text{ m})$$

The width of the facility

$$S = (0.5 \times 4047 \times 10^4)^{0.5}$$

$$= 4500 \text{ cm } (45 \text{ m})$$

Since S < 400 m, the screening technique can be used. The virtual downwind distance is

$$L_v = 113 + 1000 = 1113 \text{ m}$$

The net downwind concentration is obtained from Equation (40)

1) benzene

$$\chi = \frac{16}{2\pi(1113)} \frac{2(0.17)}{\sqrt{2\pi}\ (32)(5)} \quad (0.25) \quad = 4.9\text{x}10^{-7}\ \text{gr/ m}^3 (=0.49\ \mu\text{gr/m}^3)$$

2) trichlorobenzene

$$\chi = 1\text{x}10^{-7}\ \text{gr/m}^3 \quad (0.1\ \mu\text{gr/m}^3)$$

3) ethylene dichloride

$$\chi = 5.1\text{x}10^{-7}\ \text{gr/m}^3 \quad (0.51\ \mu\text{gr/m}^3)$$

The background concentration of each compound should be added to the results above to obtain the downwind concentrations. The estimated annual average of the downwind concentration would be higher than the net concentration given above if the the background concentration is taken into account.

At an assumed lifetime cancer risk of 10^{-5} the maximum ambient levels of each compound not allowed to exceed are obtained from Equation (42)

1) benzene

$$C_{mi} = \frac{10^{-5}}{4.8\text{x}10^{-5}} \quad = 0.21\ \mu\text{gr/m}^3$$

2) trichloroethylene

$$C_{mi} = \frac{10^{-5}}{4.2\text{x}10^{-6}} \quad = 2.4\ \mu\text{gr/m}^3$$

3) ethylene dichloride

$$C_{mi} = \frac{10^{-5}}{1.2\text{x}10^{-5}} \quad = 0.83\ \mu\text{gr/m}^3$$

To account for the additive health effect of carcinogens, the sum of normalized permissible maximum concentrations (SNPMC) is determined

$$SNPMC = \frac{0.49}{0.21} + \frac{0.1}{2.4} + \frac{0.51}{0.83} = 2.99$$

The maximum allowable downwind concentrations of each compound at 10^{-5} risk are now:

1) benzene

$$\frac{0.21}{2.99} = 0.07\ \mu gr/m^3$$

2) trichloroethylene $0.1\ \mu gr/m^3$

3) ethylene dichloride $0.51\ \mu gr/m^3$

In order to meet these concentrations, the emission rates of benzene from the disposal facility should be reduced to

$$0.17 \times \frac{0.07}{0.49} = 0.024 \text{ gr/sec}$$

Or other adjustments on the emission rate of each component can be made to meet SNPMC $\lesssim$ 1. For example, if the allowable downwind concentration of benzene is doubled while that of ethylene dichloride is reduced by a factor 2, the allowable concentration should be

1) benzene $0.14\ \mu gr/m^3$

2) trichloroethylene $0.1\ \mu gr/m^3$

3) ethylene dichloride $0.25\ \mu gr/m^3$

$$SNPMC = \frac{0.14}{0.21} + \frac{0.1}{2.4} + \frac{0.25}{0.83} \cong 1$$

Hence the emission rate of each compound should not exceed

1) benzene $0.17 \times \frac{0.14}{0.49} = 0.05$ gr/sec

2) trichlorobenzene 0.034 gr/sec

3) ethylene dichloride $0.18 \times \frac{0.25}{0.51} = 0.09$ gr/sec

5. Consideration of Other Health Criteria

Ambient air monitors are installed to monitor the effect of a treatment facility on the ambient air concentration of cyanides. The treatment facility is a 0.25 acre agitated lagoon. The average concentration of cyanides in the form of hydrogen cyanide in the lagoon is about 2000 mg/L. Estimate the impact of the facility on the downwind monitor when the average wind velocity is 5 m/s (stability class = D). Additional information obtained is:

Background cyanide concentration in the ambient air = 0.1 $\mu gr/m^3$.

Distance of lagoon to the downwind monitor = 200 m.

Effective zone of turbulence = 5 %.

Average temperature = $25^{o}C$.

Calculations similar to Example 1 can be used to estimate the overall mass transfer coefficient(MW of HCN = 27).

i) Convective zone

a) Liquid Phase

$$k_{L,i} = \left(\frac{32}{27}\right)^{0.5} \times 2.4\times10^{-5} = 2.6\times10^{-5} \quad \frac{gr\text{-}mol}{cm^2\cdot sec}$$

b) Gas Phase

$$k_{g,i} = \left(\frac{18}{27}\right)^{0.335} \times 2.7\times10^{-5} = 2.36\times10^{-5} \quad \frac{gr\text{-}mol}{cm^2\cdot sec}$$

ii) Agitated zone

a) Liquid Phase

$$k_{L,i} = \left(\frac{32}{27}\right)^{0.25} (0.12) = 0.125 \quad \frac{gr\text{-}mol}{cm^2\cdot sec}$$

b) Gas Phase

$$k_{g,i} = \left(\frac{18}{27}\right)^{0.25} \times 4.6\times10^{-4} = 4.16\times10^{-4} \quad \frac{\text{gr-mol}}{\text{cm}^2\cdot\text{sec}}$$

The vapor-liquid equilibrium constant, K_i, for HCN in aqueous solution is estimated by

$$K_i = \frac{\gamma_i \; P_i^o}{P}$$

The vapor pressure of HCN at 25°C = 735 mmHg from a handbook, and $\gamma_i \cong 1$ will be used for the dilute concentration.

$$K_i = \frac{(1)\ (735)}{760} = 0.967$$

The overall liquid phase mass transfer coefficients in the convective ($(K_L)_c$) and turbulent ($(K_L)_T$) zones are obtained from Equation (2)

$$\frac{1}{(K_L)_c} = \frac{1}{2.6\times10^{-5}} + \frac{1}{0.967\times2.36\times10^{-5}} = 8.23\times10^{4}$$

$$(K_L)_c = 1.22\times10^{-5} \quad \frac{\text{gr-mol}}{\text{cm}^2\cdot\text{sec}}$$

$$\frac{1}{(K_L)_T} = \frac{1}{0.125} + \frac{1}{0.967\times4.16\times10^{-4}} = 2.49\times10^{3}$$

$$(K_L)_T = 4.01\times10^{-4} \quad \frac{\text{gr-mol}}{\text{cm}^2\cdot\text{sec}}$$

The average mass transfer coefficient for the entire lagoon is obtained as follows:

$$K_L = 1.22\times10^{-5}\ (0.95) + 4.01\times10^{-4}(0.05)$$

$$= 3.16\times10^{-5}\ \frac{\text{gr-mol}}{\text{cm}^2\cdot\text{sec}}$$

The concentration of HCN in the aqueous solution is converted to mole fraction,

$$x_i = \frac{2000}{10^6} \times \frac{1/27}{1/18} = 1.33\times10^{-3} \text{ mole fraction}$$

The emission rate of HCN from the treatment lagoon is estimated from Equation (3)

$$Q_i = 27(3.16\times10^{-5})(0.25\times4047\times10^4)(1.33\times10^{-3})$$

$$= 11.5 \text{ gr/sec.}$$

Dispersion modeling will be used to estimate the impact on the downwind monitor. As in Example 4, the width of the facility is

$$S = (0.25 \times 4047 \times 10^4)^{0.5} = 3180 \text{ cm } (31.8 \text{ m})$$

Since S < 80 m where 80 m is 40 % of the 200 m, the screening technique can be used. The distance from virtual point to the disposal facility is

$$L' = \frac{31.8}{2}(5.03) = 80 \text{ m}$$

The virtual downwind distance is

$$L_v = 80 + 200 = 280 \text{ m.}$$

The net concentration impacting the downwind monitor is (Equation (40))

$$\chi = \frac{16}{2\pi\ (280)}\ \frac{2\ (11.5)}{\sqrt{2\pi}\ (8.5)(5)}\ (1) = 2\times10^{-3}\ \frac{gr}{m^3}\ \left(=2000\ \frac{\mu gr}{m^3}\right)$$

When thw wind is blowing toward the downwind monitor, the concentration at the downwind monitor is estimated to be

$$2000 + 0.1 \cong 2000\ \frac{\mu gr}{m^3}$$

The impact of the facility on the downwind population located at say 500 m from the facility can be predicted similarly. If the frequency of wind blowing toward the population is 0.25, the net concentration is

$$\chi = \frac{16}{2\pi\ (580)}\ \frac{2(11.5)}{\sqrt{2\pi}\ (18.6)(5)}\ (0.25) = 1.08\times10^{-4}\ \frac{gr}{m^3}$$

$$\left(=108\ \frac{\mu gr}{m^3} = 98\ \text{ppb}\right)$$

To evaluate whether or not this concentration is within the acceptable level recommended in the other criteria goals, the drinking water standard obtained from analysis of toxic effects data, which is protective of human health against the ingestion of contaminated water, is used. This standard is 200 μg/L. Based on daily consumption of 2 L of water and 20 m^3 of air, the acceptable ambient air concentration of cyanide is calculated as

$$\frac{200\ \frac{\mu gr}{L}\ \ 2\ L}{20\ m^3 \times 0.6} = 33.3\ \frac{\mu gr}{m^3}\ \ (=30.1\ \text{ppb by volume})$$

where it is assumed that only 60 % of the inhaled cyanide is absorbed. The average concentration impacting the population is higher than the acceptable value. The cyanide emission from the treatment facility is adversely impacting the downwind public.

NOMENCLATURE

A : surface area of disposal facility, cm^2

a_s : interfacial area per unit volume of soil for the oily waste, cm^2/cm^3

a_v : surface area per unit volume of surface impoundment, ft^{-1}

C_{ig}, C_{iL} : concentration of gas and liquid phases at the gas liquid interface in the pore, gr/cm^3

C_{iwo} : initial concentration of component i in the landfarming waste, gr/cm^3

C_{io} : concentration of component i at the soil-air interface, gr/cm^3

$C_{i\infty}$: concentration of component i in the air far away from the soil-air interface, gr/cm^3

C_i^* : concentration of component i in the air space at the immediate vicinity of the waste(or in equilibrium with the waste), gr/cm^3

C_m : maximum permissible concentration, $\mu gr/m^3$

D : diffusion coefficient, cm^2/sec (Note: D_{i,H_2O} means the diffusion coefficient of component i in water)

D_{ei} : effective diffusivity of component i in the air-filled soil pore, cm^2/sec

D_{wi} : diffusivity of component i in the waste, cm^2/sec

d : diameter of aerator turbine or impeller, ft

d_e : effective diameter of quiscent area of surface impoundment, m

d_p : soil clump diameter, cm

g : gravitational or conversion constant, ft/sec^2

H : Henry's law constant, $atm/mol/m^3$

H_c : Henry's law constant in concentration ($C_{ig} = H_c\, C_{iL}$)

H_o : effective depth of surface impoundment, ft

h : depth of soil cover, cm

h_{eq} : soil equivalent to polyethylene film

h_f : polyethylene film thickness, cm

h_p : depth of penetration by soil contamination below the surface, cm

h_s : depth of subsurface injection, cm

J : oxygen transfer rating of surface aerator, normally about 3 lb O_2/hr-hp

K : vapor-liquid equilibrium constant

K_L : overall mass transfer coefficient, gr-mol/cm^2·sec

k_g, k_L : gas and liquid phase mass transfer coefficients, resp., gr-mol/cm^2·sec

$k_{g,i}$: gas phase mass transfer coefficient of component i in air, gr-mol/cm^2·sec

$k_{L,i}$: liquid phase mass transfer coefficient of component i a disposal facility, gr-mol/cm^2·sec

L : distance from center of a disposal facility to property line, m

L_v : virtual downwind distance to receptor ($L' + L$), m

L' : distance from virtual point to center of a disposal facility, m

M_T : amount of waste application, gr

m_{io} : initial amount of component i placed for landfarming, gr

MW : molecular weight

N_{FR} : Froude number, $d\,\omega^2/g$

N_p : power number, $P_r\, g/\rho_L\, d^5\, \omega^3$

N_{Re} : gas Reynolds number, $\rho_g\, d^2\, \omega / g\, \mu_g$

N_{SC} : gas Schmidt number, $\mu_g\, g/\rho_g\, D_{i,air}$

p : partial pressure, mmHg

P : total pressure, mmHg

P^o : pure component vapor pressure, mmHg

P_a : air-filled porosity, cm^3/cm^3

P_T : total porosity, cm^3/cm^3

POWR : total power input to aerators in the aerated surface impoundment, Hp

P_r : power to impeller, ft·lb force/sec

Q : rate of emissions from a disposal facility, gr/sec

q : emission rate per unit area of the area source, gr/cm^2·sec

R : gas constant, cm^3·mmHg/ ^oK·mol

$\overset{*}{Re}$: roughness Reynolds number (See Reference 4 for the expression)

Ru : unit risk

S : width of area source, m

T : temperature, ^oK

t : time, sec

t_d : dry-out time, sec

U_o : surface velocity, ft/sec, normally 0.035 x wind speed(ft/sec) for natural surface, ft/sec, and 0.1 ft/sec for outside of region of effect of aerators in the biological treatment.

u : wind speed, m/sec

U_{air} : wind speed, m/hr

V : volume of surface impoundment, ft^3

$\bar{V}$: average gas velocity in the soil pore in the upwind direction, cm/sec

w : soil water content, gr/gr

w_f : fraction of oil in film form on soil

x : liquid phase mole fraction

y : gas phase mole fraction

z_o : oil layer diffusion length, cm

Greek Letter

α : oxygen transfer correction factor

μ : viscosity, lb-f·sec/ft^2

χ(chi) : net ambient concentration of a hazardous substance originated from disposal facility emissions, gr/m^3

σ_z : standard deviation of the concentration distribution in the vertical direction, m

ϕ : relative frequency of occurrence from stability wind rose

θ : temperature, ^oC

γ : activity coefficient

ρ : density, lb/ft^3

$\bar{\rho}$: density, gr/cm^3

ω : rotational speed of turbine impeller, rad./sec

Subscript

air : air

c : convective

H_2O : water

g : gas

i : hazardous component i

j : hazardous component j

L : liquid

O_2 : oxygen

p : soil particle

T : turbulent

Tol : toluene

w : waste

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APPENDICES

Appendix A

Methods for Determining K-values

1. From Experimental Data:

The liquid sample taken from a surface impoundment can be equilibrated in a head space, and the liquid and vapor phases can be analyzed for concentrations of each hazardous component. The K-value is

$$K = y_i / x_i \qquad (A-1)$$

where K is the K-value or the vapor-liquid equilibrium constant, y_i is the mole fraction of hazardous component i in the vapor phase, and x_i is the mole fraction of hazardous component i in the liquid phase. When the partial pressure(p_i, mmHg) of component i in the vapor phase is measured, $y_i = p_i/P$ where P is the total pressure, mmHg.

The K-values determined this way are valid at the applicable liquid concentrations and temperature. If Henry's or Raoult's laws hold for the liquid mixtures, the K-value could be used over a range of concentrations.

2. From Henry's Law Constant:

Henry's law often holds for aqueous solutions of sparingly soluble organic compounds. Examples are benzene, chloroform, etc. in wastewater. Henry's law constants are expressed in several different units. A collection of Henry's law constants in atm/(mol/m^3) is attached herewith(Table A-1). Other Henry's law constants may be found in a handbook. The K-value can be determined by one of the following ways:

$$K = \frac{H\left(\frac{atm}{mol/m^3}\right) \times 10^6}{P(atm)\ \ MW_{av.}} \qquad (A-2)$$

or

$$K = \frac{H\left(\frac{\text{atm}}{\text{mol/m}^3}\right)}{R\left(\frac{\text{m}^3\ \text{atm}}{\text{mol}\ {}^\circ\text{K}}\right) T({}^\circ\text{K})} \quad \frac{C_{liquid}\left(\frac{\text{lb-mol}}{\text{ft}^3}\right)}{C_{gas}\left(\frac{\text{lb-mol}}{\text{ft}^3}\right)} \qquad \text{(A-3)}$$

where P is the total pressure, atm, $MW_{av.}$ is the average molecular weight of solution, R is the gas constant(8.2×10^{-5} $\frac{\text{m}^3\ \text{atm}}{\text{mol}\ {}^\circ\text{K}}$), T is the temperature, $^\circ$K, C_{liquid} is the liquid density, lb-mol/ft^3, and C_{gas} is the gas density, lb-mol/ft^3.

Example

Henry's law constant for benzene in water is 5.55×10^{-3} atm/(mol/m^3) at 25 $^\circ$C. Calculate the K-value by Equations (A-2) and (A-3).

1) Equation (A-2)

$$K = \frac{5.55 \times 10^{-3} \times 10^6}{(1)\ (18)} = 308.3$$

2) Equation (A-3)

$$C_{liquid} = 62.4/18 = 3.467 \text{ lb-mol/ft}^3$$

$$C_{gas} = \frac{P}{RT} = \frac{14.7}{10.73(460+77)} = 0.00255 \text{ lb-mol/ft}^3$$

$$K = \frac{5.55 \times 10^{-3}}{8.2 \times 10^{-5}(298)} \quad \frac{3.467}{0.00255} = 308.5$$

3. From Raoult's Law

Raoult's law often holds for hydrocarbon mixtures. The K-value can be calculated by

$$K = \frac{P_i}{P} \qquad \text{(A-4)}$$

where P_i is the vapor pressure of a hazardous component at a temperature of concern, mmHg, and P is the total pressure.

3. Other cases:

When Henry's law constants are not available or the Raoult's law does not hold for the mixture, the K-value can be obtained by

$$K_i = \frac{\gamma_i P_i}{P} \qquad (A\text{-}5)$$

where γ_i is the activity coefficient, P_i is the vapor pressure of a hazardous component, mmHg, P is the total pressure, mmHg. There are methods of determining the activity coefficients for aqueous solutions and hydrocarbon mixtures. These methods are not discussed here. If γ is close to unity as in the case of hydrocarbon mixtures, Equation (A-5) becomes Raoult's law. If γ is not close unity but remains constant at low concentrations, Equation (A-5) becomes Henry's law.

4. Henry's law constant in concentration:

The Henry's law constant (H_c) expressed in concentration unit occurs in problems involving landfarming. The constant is related by

$$C_{ig} = H_c \, C_{iL} \qquad (A\text{-}6)$$

where C_{ig} (gr/cm^3) and C_{iL} (gr/cm^3) are concentrations on the gas and liquid side of the oil-air interface in the soil pore spaces. H_c is related to H or K as follows:

$$H_c = H \left(\frac{\text{atm}}{\text{gr-mol/m}^3} \right) C_g \left(\frac{\text{gr-mol}}{\text{cm}^3} \right) \frac{10^6}{P(\text{atm})} \qquad (A\text{-}7)$$

and

$$H_c = K \, C_g \left(\frac{\text{gr-mol}}{\text{cm}^3} \right) \frac{MW_{av.}}{\bar{\rho}_w} \qquad (A\text{-}8)$$

where C_g is the molar density of vapor($1/2.44 \times 10^4$ gr-mol/cm^3), $MW_{av.}$ is the average molecular weight of the oil, and $\bar{\rho}_w$ is the density of the oil, gr/cm^3.

Table A-1. Henry's Law Constants

Compound	Temp. ^{o}K	Molecular Weight g/mol	H, m^3 atm/mol x 10^{-3} Calculated	Experimental
Acenaphthene	298	154.2	- -	0.241
Benzene	298	78.1	5.48	5.55
Carbon tetrachloride	298	153.8	28.6	30.2
Chlorobenzene	298	112.6	3.70	3.93
1,2,4-Trichlorobenzene	-	181.5	2.32	1.42
Hexachlorobenzene	298	284.8	- -	1.70
1,2-Dichloroethane	298	99.0	1.35	1.10
1,1,1-Trichloroethane	298	133.4	4.08	4.92
Hexachloroethane	295	236.7	- -	9.85
1,1-Dichloroethane	293	99.0	5.54	5.45
Chloroform	298	119.2	3.23	3.39
1,2-Dichlorobenzene	298	147.0	2.00	1.94
1,3-Dichlorobenzene	298	147.0	2.96	2.63
1,4-Dichlorobenzene	298	147.0	- -	2.72
1,1-Dichloroethylene	293	97.0	15.1	15.0
1,2-trans-Dichloroethylene	293	96.9	4.05	5.32
1,2-Dichloropropane	293	113.0	2.75	2.82
1,3-Dichloropropylene	298	111.0	1.35	3.55
Ethylbenzene	298	106.2	6.44	6.44
Methylene chloride	298	84.9	3.04	3.19
Bromoform	298	252.8	0.595	0.532

Compound	Temp. °K	Molecular Weight g/mol	H, m^3 atm/mol x 10^{-3} Calculated	Experimental
Bromodichloromethane	-	163.8	- -	2.12
Trichlorofluoromethane	298	137.4	104	58.3
Dibromochloromethane	-	168.8	- -	0.783
Hexachlorobutadiene	293	260.8	25.7	10.3
Hexachlorocyclopentadiene	298	272.7	36.2	16.4
Nitrobenzene	298	123.1	0.023	0.024
4,6-Dinitro-o-cresol	-	198.1	- -	0.0014
Phenol	298	94.1	- -	0.0013
Acenaphthylene	298	152.2	- -	0.114
Fluorene	298	116.2	- -	0.117
Tetrachloroethylene	298	165.8	28.5	28.7
Toluene	298	92.1	6.44	5.93
Trichloroethylene	298	131.5	11.7	11.7
Aldrin	293	364.9	- -	0.496
Dieldrin	298	380.9	- -	0.058
Chlordane	298	409.8	- -	0.048
Heptachlor	298	373.4	- -	1.48
Heptachlor epoxide	298	389.3	- -	0.032
Arochlor 1254	298	328.4	- -	8.37
Toxaphene	298	413.9	- -	4.09

APPENDIX B

DRAFT

A MODEL FOR VOLATILE CHEMICAL EMISSIONS TO AIR FROM LANDFARMING OF OILY WASTES

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An overview of petroleum industry landfarming operations for disposal and treatment of organic waste was given by Knowlton and Rucker (1). The land is cultivated to provide a continuing supply of oxygen. Water and fertilizer are added, if needed. The end products of landfarming are carbon dioxide, water, and increased humus content of the soil. The most common wastes treated within the petroleum industry are oily sludges and biosolids.

Typically a heavy oily sludge is spread several inches thick. The soil is then cultivated at frequent intervals for about two months. Vacuum trucks apply free flowing oil waste directly to the land. Heavy, solidified wastes are distributed over the landfarm from dump trucks and spread with a bulldozer. Cultivation of the waste into the soil is done with various kinds of farm implements.

Application rates vary widely from 200 to more than 600 barrels per acre per year. The application thickness can vary from several inches to a thin layer of a fraction of an inch. Avoiding clumps and spreading as a uniform layer as possible makes subsequent cultivation most effective. The cultivation depth is usually the top six inches of soil. Refinery waste suitable for landfarming are: tank cleanings with 20 to 50 percent oil, separator cleanings with 10 to 20 percent oil, other cleanings with approximately 10 perce oil, a wastewater treatment plant sludge zero % and filter clays with approximately 8 percent oil.

To evaluate the extent of atmospheric emission of volatile chemicals from landfarming oprations transport mechanisms from the soil surface and the soil pore spaces must be considered. During the time the oily waste is placed upon the soil and cultivated,

vaporization can occur directly from the surface. The exposed liquid or semi-solid contains volatile component i of mole fraction x_i. The vapor concentration, C_i^* of this chemical in equilibrium with the oily waste is:

$$C_i^* = \frac{\gamma_i P_i^o MW_i}{R T} \qquad (1)$$

where MW_i is molecular weight of the volatile chemical, P_i^o is pure component vapor pressure, γ_i is the liquid phase activity coefficient, R is the gas constant and T is absolute temperature. The flux rate from the surface is:

$$q_i = k_{g,i} C_i^* MW_i \qquad (2)$$

where q_i is in $gr/cm^2 \cdot s$, $k_{g,i}$ is the gas phase mass transfer coefficient in $gr\text{-}mol/cm^2 \cdot sec$ and C_i^* is in gr/cm^3. The rate equation assumes no mass transfer resistance in the oil phase. This assumption will be valid only for a very short period of time, as the volatile chemical species is lost from the surface molecules need to be replaced from the lower liquid layers and hence the resistance increases. Eq. (2) however, provides an estimate of the maximum volatilization rate. See Thibodeaux (2) for the development of a model for the evaporation of liquid chemicals spilled or otherwise placed on land.

Soil Pore-space Evaporation and Diffusion Model

A model for the vaporization and movement of pure liquid spilled on a dry soil has been presented by Thibodeaux (3). The pure liquid is assumed to soak into the dry soil and contaminates it to a depth h_p. The liquid coats the pore walls and particle junction sites. The chemical evaporates from the interstitial soil surfaces,

and the vapor diffuses through the pores upward toward the air-soil interface. In a very short time a hypothetical "dry" zone develps near the surface, and liquid vaporization occurs from the plane formed between this zone and the remaining "wet" zone. As vaporization occurs the dry zone increases in depth and the wet zone decreases. It is further assumed that the soil column is isothermal, that no vertical liquid movement occurs by capillary action, no adsorption on soil particles, and no biochemical oxidation. Equations are developed for the evaporation life time and flux rate. This paper extends the model to the evaporization of chemical species from oil waste mixture in landfarm-type treatment type operations.

Oily wastes are placed on the soil surface or injected below the surface. When placed on the surface the waste is then cultivated into the soil column to the depth of the plow slice h_p(cm). Subsurface injection is done to a depth below the surface h_s (cm), where $h_s \leq h_p$. Figure 1 shows these depths and the relative locations of the "wet" and "dry" zones for volatile species i in the oily waste. The following is a general model which applies to either the surface application or subsurface injection method.

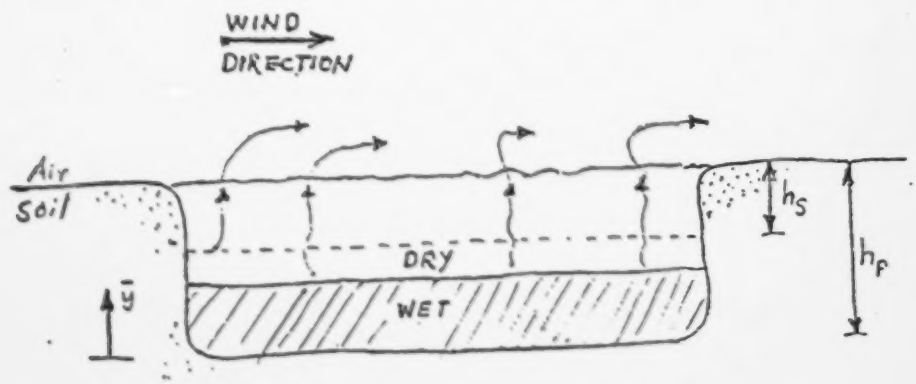

Figure 1 Evaporation and Diffusion from landfarm Soil

Species i in the oily waste mixture exerts a concentration C_{ig} (g/cm^3) while in the wet zone the evaporation diffusion life time t_d for initial mass of i m_{io}(g) incorporated into the zone $h_p - h_s$ is

$$t_d = (h_p + h_s)\, m_{io}/(2\, D_{ei}\, A\, C_{ig}) \qquad (3)$$

where D_{ei} (cm^2/s) is the effective diffusivity of i in the air-filled soil pore species and A(cm^2) is the surface area over which oily waste is applied (i.e., m_{io}/A is the application rate). The flux rate, q_i($g/cm^2 \cdot s$) through the wet-dry interface is

$$q_i = D_{ei}\, C_{ig} / \left[h_s^2 + 2\, D_{ei}\, t\, A\, (h_p - h_s)\, C_{ig}/m_{io}\right]^{1/2} \qquad (4)$$

where t is the time after application. For the surface application case h_s=0 in equations 3 and 4. In both cases $t \leq t_d$.

The effective wet zone pore space concentration of species, i, C_{ig} must reflect the diffusion resistance within the oil phase and within the airfilled pore spaces. The rate i moves through the oil phase in the wet zone is equal to the rate i moves from the top of the wet zone to the surface. This equality is:

$$a_s\, A\, \bar{y}(D_{wi}/z_o)(C_{iwo} - C_{iL}) = (D_{ei}\, A/(h_p - \bar{y}))(C_{ig} - 0) \qquad (5)$$

where a_s (cm^2/cm^3) is the interfacial area per unit volume of soil for the oily waste, D_{wi} (cm^2/s) is the effective diffusivity of i in the oil. z_o(cm) is the oil layer diffusion length, and C_{iwo}(gr/cm^3) is the initial concentration of i in the oil. For equilibrium at the interface

$$C_{ig} = H_c\, C_{iL} \qquad (6)$$

where C_{ig} (g/cm^3) and C_{iL} (g/cm^3) are concentrations on either side of the interface, and H_c (cm^3 oil/cm^3 air) is the Henrys law constant in concentration form. Combining Equations 5 and 6 yields;

$$C_{ig} = \left[\frac{H_c}{1 + H_c \left(\frac{D_{ei}\, z_o}{D_{wi}\, a_s\, f(\bar{y})}\right)}\right] C_{iwo} \qquad (7)$$

where $f(\bar{y}) = \bar{y}\,(h_p - \bar{y})$ accounts for the lenthening dry zone. The average value of this function during the evaporation diffusion process is

$$f(\bar{y}) = (h_p^2 + h_p\, h_s - 2\, h_s^2)/6 \qquad (8)$$

and should be used to estimate $f(y)$ in Equation (7). For small values of the oil layer coating the soil particles, z_o, or large interfacial area, a_s, Equation 7 reduces to $C_{ig} = H_c\, C_{iL}$ and the process is air pore space diffusion controlled.

Oil mass distribution within the soil column will be assumed to be bidispersed. One fraction of the mass, $f\, m_{io}$, is in "film" form. This fraction, a thin film that coats the soil clumps, is in direct contact with the air filled pore spaces and is readily available for transport to the surface. The remaining mass is in "lump" form and is $(1-f)m_{io}$. The lump fraction is contained in the dead-end air-filled pore spaces or in the spaces between soil particles. The lumps are relatively large and have low interfacial area so that molecules of i have a more tortu path to the air-filled pore spaces that connect with the surface. Figure 2 shows the bidispersed nature of oil in a soil column. Since approximately half of the pore spaces in soil are air filled (4), f=0.5 seems reasonable as a first approximation.

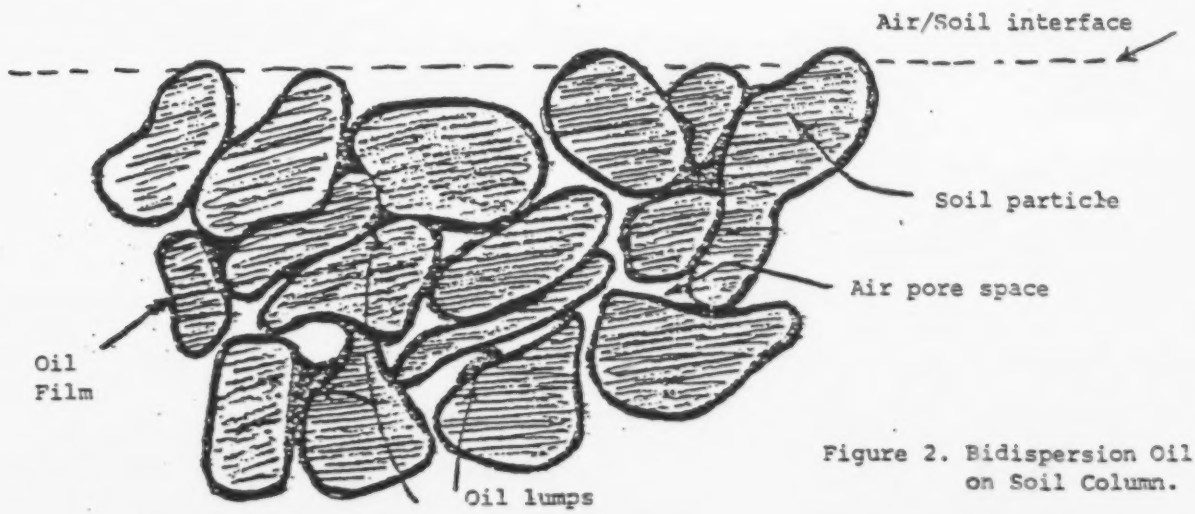

Figure 2. Bidispersion Oil on Soil Column.

Soil with a high degree of organic matter is usually found to have a structure classed as spheroidal clumps (4). These clumps are reported to have diameters up to one half inch. By using spheres and associations of spheres it is possible to construct simple geometric models and estimate the oil phase diffusion path, z_o(cm), and the interfacial area per volume, a_s (cm^2/cm^3), for the film and lump oil forms.

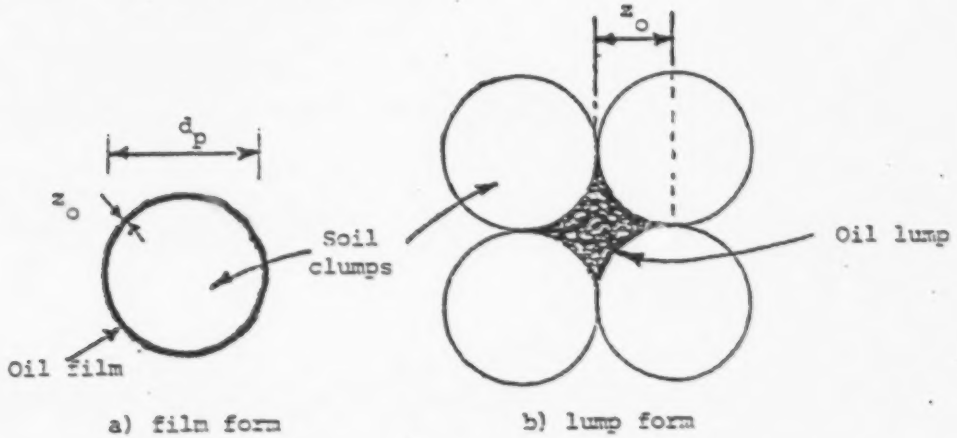

Figure 3. Sphere Models for Oil Forms in Soil.

Figure 3 shows simple sphere models for oil forms in the soil column.

For oil in film form the thickness or diffusion path length, z_o (cm), is

$$z_o = d_p \bar{\rho}_p w_f / 6 \bar{\rho}_w \qquad (9)$$

where d_p(cm) is soil clump diameter, $\bar{\rho}_p$ (g/cm^3) is soil clump density, w_f is the fraction of oil in film form on the soil, and $\bar{\rho}_w$ (g/cm^3) is the oil density. The interfacial area for the film form is;

$$a_s = 6/d_p \qquad (10)$$

For oil in lump form the mass will be assumed to be trapped in the space formed by eight spheres in an orthogonal arrangement. Figure 3 shows a two-dimensional view of the lump form model. For diffusion path length for the lump is:

$$z_o = d_p/2 \qquad (11)$$

and the a_s for the lump is:

$$a_s = 2.70/d_p \qquad (12)$$

In the case of bidispersed oil the model equations developed for evaporation and diffusion (i.e., Equations 3,4,7 and 8) apply for each form. Because of relative diffusion path lengths and interfacial areas the dry zone for the film mass fraction will grow faster than that for the lump mass fraction. In other words the life-time for dry-out will be shorter for the film form. The volatile component i in the film form will contribute to initial high flux rates of relative short duration. This is because z_o is small and a_s is large. Volatile component i in lump form will have lower flux rates and larger life-time. This is due to large z_o and lower a_s values. The net result is high initial flux rates contributed to by both oil forms. The average flux rate during time period t is twice the point rate value obtained by Equation 4. The point rate falls as the square root of time. The film form does not contribute to the flux when $t > t_f$. The flux continues to fall until $t = t_L$ (i.e., lumps life-time). The air filled pore spaces still contain vapor of i and this remaining small quantity moves to the surface by vapor diffusion. Thibodeaux (3) presents a model rate edquation that is exponential in form for this period. The time for depleting the soil air filled pore spaces of 90% of the

remaining vapor is

$$t_{0.1} = 0.794\, h_p^2 / D_{ei} \qquad (13)$$

The model is capable of handling the emission of multiple volatile components from the oil. This can be done by treating each component individually using the model equations and assuming no interaction or interference between species. The total flux rate is the sum of the individual species flux rates. The total flux for surface application should decrease as $\sqrt{t}$ just as for individual species.

The re-cultivation of the waste treatment area sometime after the first application may result in a temporary increase in the vapor emission rate. If the area is plowed after a period of time t (s) and this period is less than the life-time of species in either film or lump form, the remaining masses in the wet zones are uniformly redistributed in the plow slice. The mass of i, $m_{i\bar{t}}$ (g), volatilized during the period $\bar{t}$ is;

$$m_{i\bar{t}} = 2\, A\, \bar{t}\, q_{i\bar{t}} \qquad (14)$$

where $q_{i\bar{t}}$ ($g/cm^2.S$) the flux rate of species i at $t=\bar{t}$. The remaining mass, $m_{io}-m_{i\bar{t}}$, is now used in the model equations to compute the flux rates after plowing. The remaining mass contains the initial film and lump from distribution.

Preliminary results from laboratory simulation experiments of landfarming volatile emissions(5) suggests that the model is qualitatively reasonable. Equation 4 shows that concentration in the air above an area, treated by surface application then cultivated, should fall with the $\sqrt{t}$. Emission data where concentration in the air from a laboratory simulation is measured with time should have

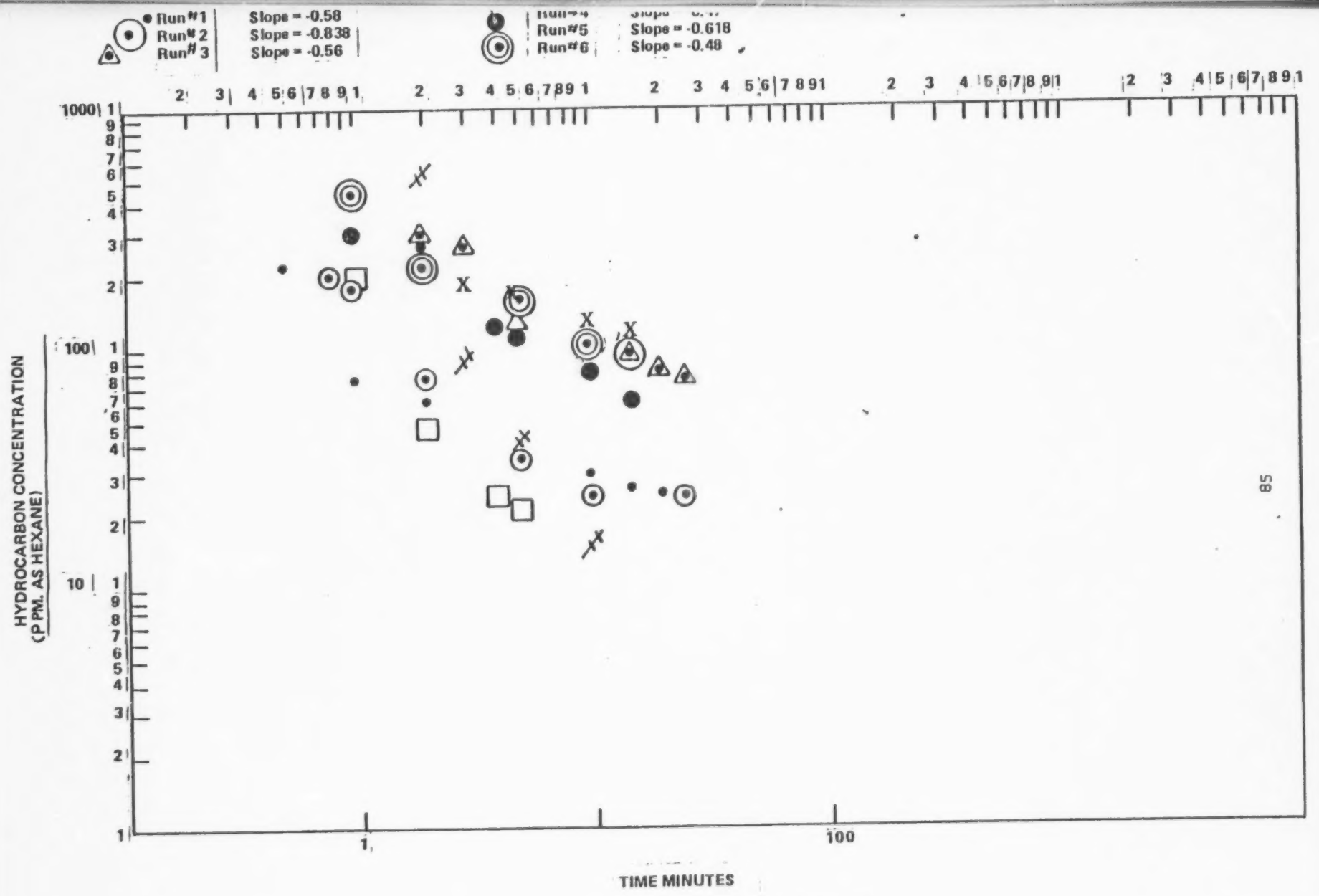

FIGURE 4. CONC. vs TIME

a slope of -0.5. Figure 4 shows the analyzis of some preliminary data for eight experiments. The average slope is -0.68 with a range of -0.39 to -1.3.

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